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OF

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LABORATORY METHODS
OF
INORGANIC CHEMISTRY

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BY
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AUTHORS' PREFACE.

THIS book outlines a course of laboratory work which is essentially synthetic in nature and is designed to aid in acquiring a more adequate knowledge of inorganic chemistry than is to be obtained by practice in chemical analysis alone. The need of supplementing the work of analytical chemistry in such a way has indeed been recognized in most chemical laboratories of the German technical schools and universities, in fact such instruction still persists as a part of the classic method of teaching chemistry. To-day a training according to these lines is considered desirable even for those students with whom chemistry is a minor subject. It has been the aim of the authors to enlarge the choice of suitable experiments by publishing the procedures which they have tested and found satisfactory in their own laboratories in the course of a number of years' experience.

The experimental part of the book is given in relatively complete detail, because in our opinion this does not materially lessen the self-reliance of the student, who has, as a rule, but a limited time at his disposal. The beginner obtains ample opportunity for acquiring manipulative skill and for exercising ingenuity, in the carrying out of the work and in modifying and improving the directions to correspond to the facilities at hand; others who need particular preparations as starting material for further investigation can appreciate directions in which technical difficulties are guarded against.

To aid in the study of the theoretical relations brief general discussions are interspersed throughout the book as well as references to the original literature and the text-books of inorganic and theoretical chemistry which should be freely consulted.

As regards the arrangement of the material, we have departed from the disposition which is common to-day of treating the compounds in connection with the groups of elements. We have chosen to base the classification upon the different *types of*

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combination, and thereby have returned to the older usage. Among the early authors Thénard in 1813 writes: "*La méthode, que j'ai constamment suivie, consiste à procéder du simple au composé, du connu à l'inconnu, à réunir dans un même groupe tous les corps analogues, et à les étudier d'abord d'une manière générale et ensuite d'une manière particulière.*" Gmelin in 1817, however, took a different stand and in his "Handbuch" arranged the compounds according to the elements, and thus introduced the system of classification which has been followed by nearly all of his successors. Even to-day Gmelin's reasons for departing from the older method of treatment probably hold equally well as regards elementary books for beginners; the older method scatters the compounds of a single element in such a way that the student fails to get a distinct, coherent picture. This book, however, is intended primarily for those who have passed beyond the more elementary stage in their study of chemistry, so that it does not seem to us to be too daring to make the experiment as to how well our modern, inorganic chemistry will fit into the older framework. It seems as if thereby, aside from the old advantage of a better comprehension of analogous methods of preparation and analogous properties, there results a particularly intimate amalgamation of experimental and theoretical chemistry, for in this way we advance, as it were, from a "one component system" to one of "several components." A similar return to the older method of classification is to be found, for example, in the second part of the Modern Chemistry by Sir W. Ramsey; in the arrangement adopted by A. Werner and P. Pfeiffer in the Inorganic Abstracts in R. Meyer's Jahrbuch der Chemie; and in A. Werner's Neuere Anschauungen auf dem Gebiete der anorganischen Chemie. This system was also outlined by one of us in a lecture on *Complex Compounds* delivered in Göttingen in 1903–1904.

The method of arrangement chosen often separates preparations which are closely related to one another, as for example where one is used as starting material for the formation of the other; to show these relations the "Dependent Preparation" is noted at the end of many of the procedures. In the last chapter, which treats of compounds of the rarer elements, we have departed from our chosen system of classification because in this case the question of raw material for the preparation of the individual compounds is of chief importance, and here the characterization of the element in question is at present of more importance than the type of combination.

The instructor will at once notice on glancing through these pages that for a rapid and successful carrying out of the processes certain requirements are to be met as regards apparatus and laboratory facilities; these should at all times be available for the student's use.

The experiments necessary for working out and testing the methods prescribed were carried out during the last eight years with the aid of students at the University of Kiel, and to some extent at the Universities of Göttingen and Clausthal. Published processes have frequently been changed or improved according to our experience, though no doubt it will still be found that the directions and yields can be further improved.

TRANSLATORS' PREFACE.

For some time previous to the appearance of the German edition of this book, the translators had been convinced of the value of laboratory work in Inorganic Preparations as a basis for the teaching of the general principles of chemistry. In fact one of the translators had just published a more elementary text of this character which was designed especially for first-year students at the Massachusetts Institute of Technology.[1]

The German text has, in the main, been faithfully followed, although a few minor changes have been made to adapt the book for the use of English-speaking students. The German authors have not only coöperated by carefully reading the proof sheets but they have also furnished the revisions and additions which they intend to incorporate in the Second German Edition.

The book applies especially to the more advanced college or university students who would broaden the scope of their training in inorganic chemistry beyond that obtained from courses in qualitative and quantitative analysis. It might be studied with equal advantage, simultaneously with, or following, the more advanced work in analytical chemistry.

In addition to the usefulness of this book to students, it should prove of value to manufacturing chemists, for although the working directions in the book are given for preparations strictly on the laboratory scale, still the direct bearing of the principles and theories of physical chemistry upon the efficiency of the chemical processes is brought out in a manner which would apply on a large as well as on a small scale.

The second edition contains numerous changes that have been made in the third and fourth editions of the German text as well as some other improvements, including a discussion of the periodic classification of the elements.

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[1] Blanchard and Phelan: Synthetic Inorganic Chemistry, Third Edition, 1924.

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LABORATORY METHODS
OF
INORGANIC CHEMISTRY.

INTRODUCTORY REMARKS ON LABORATORY PRACTICE.

1. Heating.

For heating and melting solid substances crucibles made of porcelain, difficultly-fusible clay, or iron are used. Small crucibles may be heated with a Bunsen burner (700°) or, for higher temperatures, with the Müncke, Méker or Teclu burner (800°) or over a blast lamp; for long heating with the latter it is sometimes convenient to have a water pump arranged to furnish an air blast. In order to obtain a uniform temperature of about 1000° small crucibles may be surrounded with a clay mantle or a gas muffle furnace can be used. Larger crucibles can be placed inside a piece of iron stovepipe or an inverted flowerpot with its hole enlarged. Large crucibles may be heated reasonably hot with a Fletcher burner by using such an insulating mantle to prevent some of the loss of heat by radiation; or to about 1200° in a gas furnace.

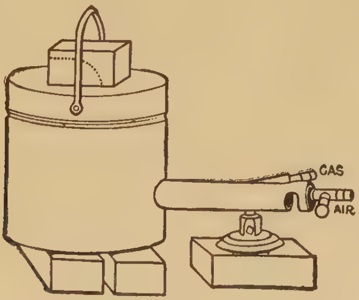

Fig. 1.

If an abundant air blast is available at a fairly steady pressure, the most convenient and useful form of furnace is the gas furnace, Fig. 1, made of fire clay supported by a casing of sheet iron, into which the flame from a large blast lamp is admitted through a hole near the bottom. In the absence of an air blast, gasolene blowpipes, similar to those commonly used by plumbers, serve almost as well as the gas blast lamps. The use of charcoal furnaces is inexpensive and to be recommended even at the present day. Such a furnace is shown in Fig. 2, one-tenth its natural size. It is made of sheet iron and is about 250 cm. high and 280 cm. wide. Larger furnaces may be built of fire brick and connected with the chimney of the building. The fire in such a furnace can be started with some glowing charcoal which has been heated before the blast lamp; the furnace is then fed with layers of charcoal and coke and finally with coke alone.

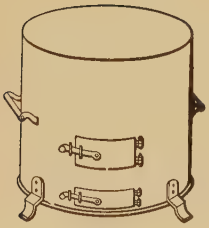

Fig. 2.

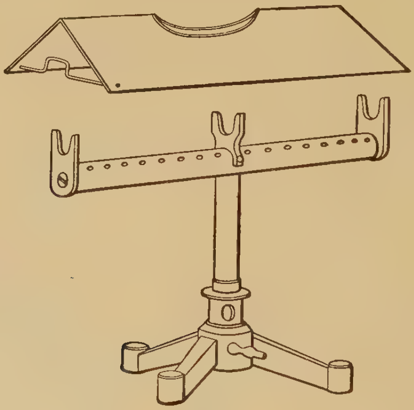

Fig. 3.

For heating substances in glass or porcelain tubes, a flame spreader placed on an ordinary Bunsen burner is used when only short lengths are to be heated; for longer stretches a row burner, as shown in Fig. 3, is employed, and to retain the heat a cover of asbestos board can be supported just above the tube by means of wires. The three supports for the tube can be protected by wrapping wet asbestos pulp about them, pressing it firmly into position and allowing it to dry. For higher temperatures over a considerable length of tube a combustion furnace, such as is used in organic ultimate analysis, is suitable. Very high temperatures may be obtained with the blast lamp if the part of the tube to be heated is surrounded by an asbestos chamber like that shown in Fig. 4. The bottom of the chamber should measure about 10 × 16 cm. and the height about 13 cm. In the bottom is a large hole for the flame of the blast lamp to enter; in the two end walls are holes through which the tube to be heated just fits. As a cover, a piece of asbestos board serves, which is loosely laid on top of the box and is provided near the four corners with round holes of 2 cm. diameter. The box is held together by means of wire fastenings. For heating long tubes to very high temperatures, a Mitscherlich tube furnace can be used which is 50 cm. long and is made of sheet iron lined with fire-clay.

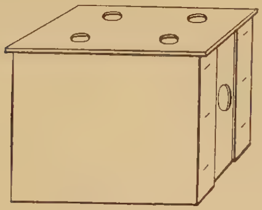
Fig. 4.

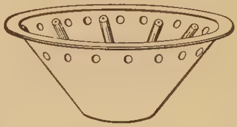
Fig. 5.

For providing and maintaining constant temperatures, up to 1500°, the platinum electrical resistance furnace, and for temperatures above 2000° the carbon resistance furnace, are invaluable. Although such furnaces would be very convenient for some of the preparations described in the following pages, they may be dispensed with on account of their high price.

Many different forms of apparatus have been devised for uniformly heating flasks and similar vessels to moderate temperatures. Besides sand baths, Babo's boiling funnel (Fig. 5), which is capable of wide application, and nickel air baths, are particularly to be recommended.

When liquids are to be boiled for a considerable length of time, the flask should be provided with a condenser or a wide glass tube held either vertically or inclined so that vapors will condense and the liquid run back into the flask. This is known as heating with a *reflux condenser*.

2. Evaporation.

Large quantities of solutions are concentrated in evaporating dishes, which give a large surface for the escape of vapors from the liquid. They should be heated, unless otherwise directed, with a free flame without wire gauze or asbestos; but the flame should never be allowed to come in contact with the dry upper part of the dish, as in that case superheating would ensue which might result in the breaking of the dish or in the decomposition of the solid material that separates on the sides. Thus as the concentration progresses the flame must be lowered or the evaporation finished on the water bath. Small quantities of liquid can also be boiled down in beakers; but if this is done it is advisable to avoid bumping by stirring or by adding to the liquid such substances as small splinters of wood, bits of unglazed porcelain, or of pumice, or, best of all, some of Siwoloboff's capillaries.[1]

3. Crystallization.

When crystals are to be obtained from a solution, it is often necessary before the evaporation is finished to filter from impurities. For this purpose an ordinary plaited filter[2] is used which is placed in a short-stemmed funnel. In case the crystals separate rapidly, a Büchner funnel with suction is employed. For strongly corrosive liquids, hardened filter paper must be used or, often better still, a felt of asbestos fibers; the latter is made by suspending the asbestos in water and pouring the suspension on to the perforated bottom of a Büchner funnel, or Gooch crucible, and drawing firmly in place by suction. Crystallization will take place *on cooling* if the solubility of the material decreases with sinking temperature, otherwise by *evaporation* at a moderate heat, or at the room temperature in a desiccator. Impure crusts tend to form around the sides of the dish at the surface of the liquid; to prevent this as much as possible, dishes with perpendicular walls (beakers or glass crystallizing dishes) should be used. If this expedient is not success ful, the crystals are collected by themselves and the crusts dissolved again in the mother liquor. By slow crystallization, especially with a deep body of solution, large crystals are obtained; by more rapid cooling, as by shaking the solution in a flask under running cold water, a crystalline meal is obtained which, because it contains less mother liquor inclosed between the crystal layers, is purer, although of less characteristic form (disturbed crystallization).

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[1] Chem.-Ztg. **19**, 304 (1895).

[2] Filters of hardened paper are more expensive and allow the filtrate to flow more slowly than those of common paper, but they retain even the finest precipitates and are thus at times indispensable.

4. Suction.

Coarse crystals can be separated from the mother liquor by sucking the mass through an ordinary funnel in which is placed a small glass marble. If a few small crystals should run through at first, the liquor containing them is poured a second time through the funnel. Even fine crystals and powdery precipitates can be filtered clear if a thin cord of asbestos fibers is laid around the marble. The suction funnels of R. Hirsch and of Büchner are also much used, for all sizes of which hardened filters, which do not, like common filter paper, lose their fibers, are to be obtained in the market.

If the material on the filter dissolves but slowly, it can be washed with water, or with the liquid used for the crystallizing medium if it is other than water; substances that dissolve more readily may be washed with suitably diluted solvents, for example, with mixtures of alcohol and water and finally with pure alcohol.

5. Distillation.[1]

For distilling ordinary liquids, *flasks* are used; for substances which solidify easily *retorts* are more suitable and these in the case of high-boiling materials, may be covered with folded asbestos paper in order to keep in the heat. The use of a condenser is usually superfluous when distilling high-boiling substances from retorts; in distilling low-boiling materials a condenser of suitable length should be joined to the distilling flask with a cork stopper (Fig. 6), although sometimes the connection is left open; or a short condenser may be slipped over the neck of the distilling flask itself and made tight with corks or with pieces of rubber tubing (Fig. 7). In the case of substances that boil somewhat higher, a glass tube about the size of one's finger simply slipped over the side arm of the distilling flask serves as an air condenser (Fig. 8). If bad smelling or corrosive gases are produced during the distillation, a suction bottle fitted to the condenser tube is used as receiver and the side arm of the bottle is connected to a tube which leads into the ventilating flue of the hood.

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[1] For fuller details regarding distillation, especially of organic liquids, see text-books on Organic Chemical Preparations.

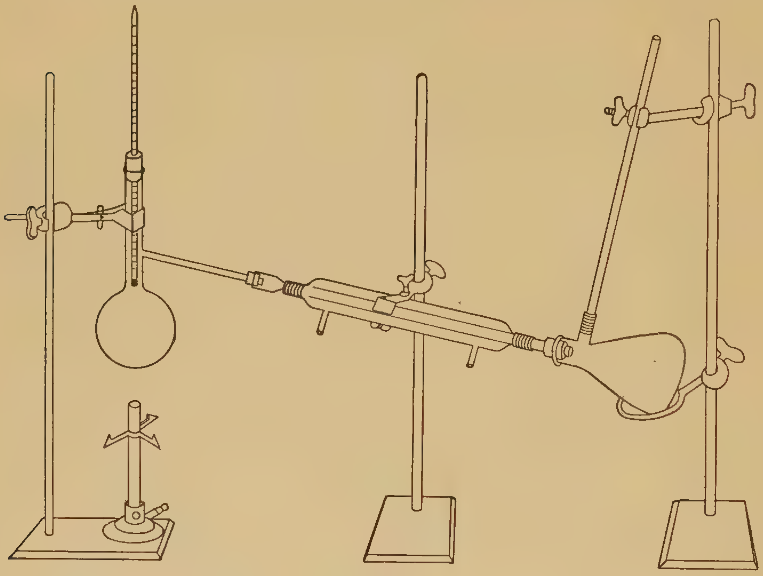

Fig. 6.

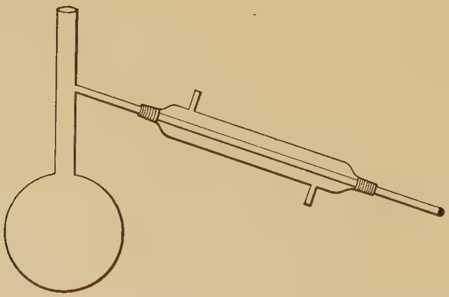

Fig. 7.

If the vapors attack cork the apparatus can be made tight with wads of asbestos fibers pressed into the joints, an expedient which often yields excellent service.

For determining the *boiling-point* of the substance a thermometer should be inserted in the neck of the distilling flask, or in the tubulus of the retort, in such a way that its bulb will be entirely surrounded by the vapors (Figs. 6 and 8); thus with a distilling flask the bulb should reach to the lower part of the neck. It is best to use thermometers so short that the mercury column will remain entirely within the vapor. The thermometer shows at the beginning a temperature somewhat too low because some time is necessary to heat it to the temperature of the vapor; toward the end the reading becomes a little too high on account of the vapor in the nearly empty flask becoming superheated. Both of these facts are to be borne in mind when judging of the purity of a substance. Concerning fractional distillation, which is seldom of importance in making inorganic preparations, see the preparation of acid chlorides and esters, Chap. VI.

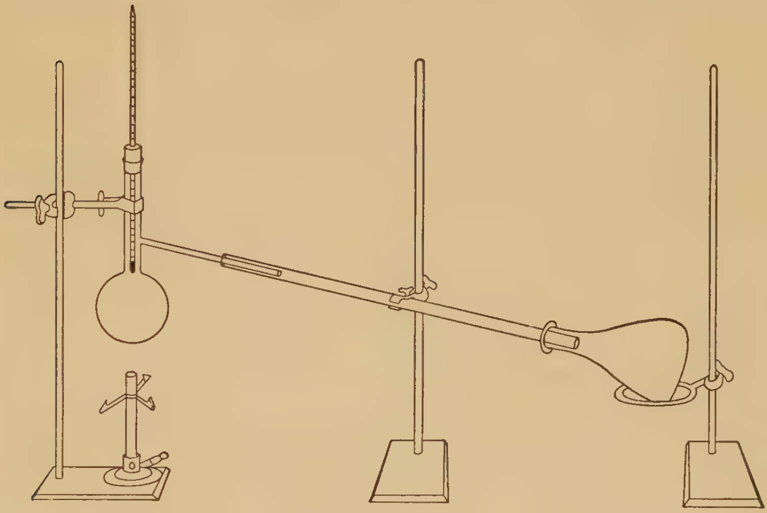

Fig. 8.

For *vacuum distillation*, use an apparatus similar to that shown in Fig. 6 on page 6. The rubber stopper of the distilling flask, besides carrying the thermometer, should be provided with a narrow piece of glass tubing, open at the top where it rises above the stopper, and at the bottom ending in a long capillary reaching nearly to the bottom of the flask. During the distillation, tiny bubbles of air enter the flask, pass through the liquid and prevent bumping. The stream of air is regulated by means of a screw clamp on a short piece of rubber tubing which is placed at the top end of the open tube. The arm of the heavy suction flask which is used as receiver should be connected with a manometer and with a suction pump. In spite of the fact that a little air is constantly entering the flask during the distillation, it is easy to get the pressure reduced to 10–18 mm. by the use of a good water pump.

Very volatile substances, such as sulphur dioxide, can be condensed in common gas wash bottles, with ground-glass joints, by means of a freezing mixture. When enough liquid has condensed in the wash bottle so that the entrance tube dips beneath its surface, the further condensation takes place very readily. If the preparation is to be preserved, it is distilled into a thick-walled glass tube, of the shape of a test tube, which is drawn down at its upper end so that when filled it can be sealed by the blast flame (Fig. 12, p. 58). Or, the substance can be poured into a sealing flask the neck of which is of about the thickness of a lead pencil, and can be readily melted together.

6. Pulverizing.

Minerals that are to serve as the raw materials for the various preparations should, if possible, be bought in powdered form, since the crushing of large masses in the laboratory is extremely laborious. If the pulverizing must be undertaken, the material should be ground in small portions and from time to time the fine powder should be sifted from the coarse by means of wire gauze or a sieve.

7. Drying of Rinsed Vessels.

When directions call for a dry vessel, it is sometimes the practice to rinse the vessel with water, then with alcohol and finally with ether, assuming that the ether will evaporate quickly and leave a dry vessel. This method is unsatisfactory. It is far better to dry the vessel, after rinsing it with several small portions of alcohol, by moving it back and forth over a small flame while applying suction through a tube reaching to the bottom of the vessel. Instead of suction, a gentle air blast can be used.

CHAPTER I.

THE ELEMENTS.

THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

The periodic recurrence of properties among the elements has been of the greatest service to the practical chemist in classifying the elements. From the very outset scientists recognized that this periodicity indicated that all elements were built up according to some definite plan out of some primordial material. Advances in knowledge during the past few decades have not, it is true, revealed the ultimate nature of this primordial material, but they have indicated very clearly some features of the systematic scheme according to which atoms of the different elements are built from electrons and protons, the atoms of negative and positive electricity.

The periodic classification of the elements becomes much more enlightening when it is arranged in accordance with our present ideas of the structure of the atom. In the following chart the number accompanying each element is the atomic number. This is approximately the serial number when the elements are arranged in the order of their atomic weights, but its deeper significance is that it represents the number of unit positive charges of the nucleus of the atom.

We will outline briefly the modern conception of the structure of the atom: Electricity, like matter, is atomic in nature and consists of two kinds of atoms, *protons* which are probably identical with the hydrogen ion (they have the mass of the hydrogen atom and the unit positive charge of the hydrogen ion) and *electrons* which are of insignificant mass $\left(\frac{1}{1840}\text{ that of the hydrogen atom}\right)$ and have an equal but opposite charge to that of the hydrogen ion.

The nuclei of atoms consist of aggregates of protons and electrons (except the nucleus of hydrogen which consists of a single proton), with the number of protons in excess of the number of electrons so that the net charge is always positive and an even

Electron Groups in Stable Kernels.		Periods Built on Stable Kernels.																
		O	1 H						1 H	2 He								
He	2	2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne								
Ne	2–8	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 A								
A	2–8–8	18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni						
Niβ	2–8–18	28 Niβ	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr								
Kr	2–8–18–8	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Cb	42 Mo	43	44 Ru	45 Rh	46 Pd						
Pdβ	2–8–18–18	46 Pdβ	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe								
Xe	2–8–18–18–8	54 Xe	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61	62 Sa	63 Eu	64 Gd	65 Tb	66 Ho	67 Dy	68 Er	69 Tm	70 Yb
Erβ	2–8–18–32–8	68 Erβ			71 Lu	72 Hf	73 Ta	74 W	75	76 Os	77 Ir	78 Pt						
Ptβ	2–8–18–32–18	78 Ptβ	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 RaF	85	86 Nt								
Nt	2–8–18–32–18–8	86 Nt	87	88 Ra	89 Ac	90 Th	91 Ux$_2$	92 U										

Symbol enclosed in heavy lines —the kernel never acquires the form of an inert gas or a beta kernel
Symbol enclosed in light double lines — the kernel sometimes acquires the form of an inert gas or a beta kernel
Symbol enclosed in a light single line — the kernel is usually or invariably of the form of an inert gas or a beta kernel

multiple of the charge of the proton. Speculations regarding the structure of the nucleus have been made in abundance but have shed little light as to the nature of the incredible forces that hold the nucleus together, — for the nuclei are almost immutable, or at least just as immutable as the elements. The nucleus possesses practically the entire mass of the atom but its bulk is excessively minute. It occupies a space in the center of the atom much as the sun does in the center of the solar system and the relative bulk is comparable.

Surrounding the nucleus are "planetary" electrons, equal in number in the neutral atom to the number of unit charges of the nucleus. These electrons are relatively as far removed from the nucleus as the planets are from the sun.

The properties of the elements, both physical and chemical, with the exception of mass, are believed to depend entirely on the arrangement of the electrons around the nucleus. Mass depends on the number of protons in the nucleus.

The arrangement of the planetary electrons is restricted to conditions imposed by the so-called "quantum" theory which deals with the relation between the emission and absorption of radiant energy and the structure of matter. There is no known law of physics which would determine the radius of the orbit of a planet. A planet might fall into any orbit whatever, depending solely on the energy it might happen to possess. Apparently the atom differs from the solar system in this respect; the quantum requirements limit the number of orbits into which the electrons may fall so that the radii (or major axes of elliptic orbits) of the possible orbits are to each other in proportion to the squares of the simple integral numbers, that is, 1 : 4 : 9 : 16 : 25 . . .

Although physicists today are rather strongly committed to the orbital theory, it may still be better to refer to the possible positions of the electrons as levels (i.e., measured out from the nucleus).

The number of electrons which can occupy each level is what determines the configuration of the atom and this in turn determines all the physical and chemical properties of the atom.

The maximum number of electrons which can occupy the succeeding levels is twice the square of the successive whole numbers or 2, 8, 18, 32, 50 . . . . The mutual repulsion of electrons, however, counteracts the tendency for the nucleus to pull the maximum number into the various levels. To take a concrete example: Xenon has an atomic number of 54, that is, the nucleus has 54 unit charges and the number of planetary electrons in the neutral atom is 54. If the attraction of the nucleus were unopposed the first three levels would be filled to 2, 8 and 18 electrons respectively and the fourth layer would hold 26. Actually the first three layers are held by the strong nuclear charge, but a fourth layer of 26 is unstable and eight are driven out into a fifth layer so that the configuration becomes Xe_{54} 2–8–18–18–8.

Now there is something inherently stable in layers having the numbers 2, 8, 18, 32 . . . and to acquire these numbers very considerable counter forces can be overcome in atom and molecule building. The Xenon atom with layers all containing the stable numbers and with the nuclear charge to just neutralize the electrons in these layers, is an extremely stable structure. This accounts for the chemical inertness of Xenon. Likewise the inertness of the other rare gases is accounted for.

Elements are known with practically all the atomic numbers from 1 to 92. With elements other than the inert gases the tendency is to acquire layers in conformity to the nearest inert gas atom, thus upsetting the electrical neutrality of the atom and giving us an "ion." Thus cesium, Cs_{55}, loses an electron and becomes a cesium ion Cs^+ when some atom such as chlorine is at hand to take on the electron.

Chlorine Cl_{17} by taking on the electron acquires the structure of argon A_{18} 2–8–8 and thus becomes a negative ion Cl^-.

The tendency for atoms to acquire an outer layer of eight where this is in any way possible is very strong. This is often accomplished as just indicated through the formation of ions, but there is another way which was first recognized by G. N. Lewis in 1916, and which in fact smooths out most of the previously irreconcilable differences between the conceptions of valence held by inorganic and organic chemists. This is that the two layers of eight may be filled by a small number of electrons simultaneously holding positions in the outer layers, or "octets," of two atoms. For example, in the chlorine molecule Cl_2 we have the two atoms Cl_{17} 2–8–7 with only 14 electrons out of which to make two octets. If two electrons are held jointly in the outer layer or "sheath" of each atom, the two octets are completed.

These electrons held in common occupy a position between the "kernels" of the two atoms and by their joint attraction for the kernels hold the molecule together.

The kernel of an atom consists of the nucleus and all of the layers except the outer layer. Those electrons in the outer layer which belong to the neutral atom itself are usually referred to as the "valence electrons."

The periods of the Periodic Classification comprise the elements coming between any two of the successive inert gases. The first two periods are short periods and comprise 8 elements each. The properties of all elements of these periods are clearly seen to be due to the tendency to revert to the structure of one or the other of the nearest inert gases. The kernels of these elements are invariable.

The elements near the beginning and end of the long periods show clearly marked similarity to elements in the similar positions in the short periods, their properties being derived from the ability of the atom to acquire the configuration of the inert gas atom. In the middle of the long periods, however, the number of electrons to be gained or lost to acquire the inert gas structure is too great. The number of electrons in the valence layer usually drops to two or three and the rest of the electrons enter some one of the kernel layers. For example, praseodymium Pr_{59} might be expected to revert to the form of Xe_{54} 2–8–18–18–8 and become quinquevalent. As a matter of fact two electrons pass into the fourth kernel layer to give Pr_{59} 2–8–18–20–8–3, the 3 electrons of the outer layer determining the valence. The tervalent ion Pr^{+++} is formed when three electrons are given to an element like chlorine. The elements praseodymium to lutecium, 59–71, constitute the so-called rare earth series. All have the nearly invariable valence of three. They differ from one another simply by one additional electron in the fourth kernel layer for each successive element. They constitute what is called a "transition series." With lutecium, however, the transition is complete and we have the structure Lu_{71} 2–8–18–32–8–3 with stable kernel layers. In the next element hafnium Hf_{72}, the additional electron has to remain in the valence layer as it cannot get into the layers containing the stable numbers of 32 or 8. Hafnium has an invariable valence of 4. Within the long periods are clearly recognizable subordinate periods which are spaced from the elements Ni, Pd, Er, Pt, in the same way that the two short periods are spaced from He and Ne. The number of electrons in each of these elements is such as might give the following structures:

Ni_{28} 2–8–18
Pd_{46} 2–8–18–18
Er_{68} 2–8–18–32–8
Pt_{78} 2–8–18–32–18

These structures possess layers of inherent stability but the nuclear charge is not great enough to hold the large outer layer of 18 or the next to last of 32 against the repulsive forces. Given the greater nuclear charge of the following atoms and these structures become stable and consequently the succeeding elements revert to those forms which are known as the beta forms or $\mathrm{Ni}\beta$, $\mathrm{Pd}\beta$, $\mathrm{Er}\beta$ and $\mathrm{Pt}\beta$, respectively, and the subordinate periods are based on these beta atoms in the same way that the major periods are based on the inert gases.

THE ELEMENTS.

Occurrence. The relative amounts of the more common elements which occur in the earth's surface, including the oceans and the atmosphere, are shown by the following table compiled from statistics by F. W. Clarke:

Oxygen.........	49.78	Magnesium.....	2.24	Barium.........	0.09
Silicon..........	26.08	Hydrogen.......	0.95	Manganese......	0.07
Aluminum......	7.34	Titanium.......	0.37	Strontium......	0.03
Iron............	4.11	Chlorine.......	0.21	Nitrogen........	0.02
Calcium........	3.19	Carbon.........	0.19	Fluorine........	0.02
Sodium.........	2.33	Phosphorus.....	0.11	Other elements..	0.48
Potassium......	2.28	Sulphur	0.11		

It is noteworthy that certain well-known elements, which are important from a purely chemical as well as from a technical standpoint, are less abundant than others that have been studied less and are regarded as "rare"; such as, for example, titanium, which is widely distributed but usually occurs only in small amounts.

The elements, with the exception of those contained in the atmosphere, sulphur, and the so-called "noble" metals, are not as a rule found in a free or uncombined state. The most important natural compounds are the oxides and sulphides (e.g., of silicon, iron, zinc, lead, antimony, mercury), the halides (e.g., of sodium, potassium, magnesium), and the salts containing oxygen (silicates, sulphates and carbonates).

Extraction. The *free elements* may be separated from one another, and from impurities, by distillation. In this way the constituents of the atmosphere have been isolated, and sulphur is obtained from the associated minerals. In other cases, the elements are dissolved out from mixtures by means of suitable solvents, e.g., gold and silver by mercury.

Oxides are Reduced. The usual reducing agents are hydrogen, carbon or carbon monoxide (No. 1), aluminium (Nos. 2 to 5), magnesium, sodium, potassium cyanide (Nos. 6 and 7), substances in solution, such as sulphurous acid (No. 8) and finally the cathodic action of the electric current, an agent of very general application. Sulphides are either changed to oxides by roasting, or they are smelted with iron whereby the metal is formed in the presence of a slag consisting chiefly of ferrous sulphide (Nos. 10, 11). Halides may be decomposed by metallic sodium or the fused salts may be electrolyzed (No. 14).

From salts containing oxygen, the elements are usually obtained by an indirect method, as for example by first forming the oxides. Examples of direct reduction, however, are the deposition of copper from copper sulphate solution by means of iron, the corresponding precipitation of silver by copper, and the preparation of phosphorus by the reduction of acid calcium phosphate with carbon at a high temperature.

REDUCTION OF OXIDES BY CARBON.

Technically, carbon is the most important reducing agent; its first product of combustion, carbon monoxide, also has a reducing power since it is readily oxidized further to carbon dioxide; in fact this latter action is often the most important, as for example in the blast-furnace process for the reduction of iron from its ores. An example of the action of carbon monoxide at lower temperatures is the reduction of gold chloride solutions (cf. No. 25). The dissociation of carbon dioxide at high temperatures, $2\ CO_2 = 2\ CO + O_2$, takes place in opposition to the combustion of carbon monoxide, $2\ CO + O_2 = 2\ CO_2$. Accurate experiments have recently shown that this dissociation becomes appreciable at above 1500° and increases rapidly with further rise of temperature, with the result that the combustion of carbon monoxide, and consequently its reducing effect, becomes diminished. This contradicts the opinion which formerly prevailed to the effect that increase of temperature always favors such technical reduction processes.

1. Lead from Lead Oxide.

Place a mixture of 50 g. litharge and 3 g. of very fine, sifted, wood-charcoal in a porcelain crucible, which is from two-thirds to three-fourths filled thereby, cover the mixture with 3 g. of powdered borax glass and heat strongly over the blast lamp. When, after about half an hour, the reduction is complete, pour the reduced lead upon an inverted porcelain crucible cover which has been previously heated so that the hot lead will not crack it.

Yield 40 to 45 g.; theoretically 46.4 g. This process is used technically for recovering lead from litharge formed in cupellation.[1]

Density Determination. Fasten a clean piece of lead weighing from 5 to 10 g. in the loop of a hair, or silk thread. Determine the weight of the lead in air (m), and the loss in weight (w) when it is entirely submerged in water; then if Q is the density of water at the temperature of the experiment[2] and $\lambda = 0.0012$ the density of air, then d, the density of the lead, is given by the following equation:

$$d = \frac{m}{w}(Q - \lambda) + \lambda.$$

The density should be computed to not more than five significant figures. The observations should be checked with the same piece of lead, or with different pieces from the same preparation. The density of lead is about 11.351.

The density of an element varies somewhat with the method of preparation. Thus with antimony distilled in vacuum, $d = 6.62$; pressed antimony, $d = 6.69$; gold distilled, $d = 18.88$, pressed at 10,000 atmospheres, $d = 19.27\frac{20°}{4°}$.

ALUMINOTHERMY.

Metallic aluminium resists the action of water and the atmosphere, not because the metal is difficult to oxidize, but on account of the fact that its surface becomes covered with a thin, coherent layer of oxide which protects it from further attack. If the formation of this layer of oxide upon the aluminium is prevented by amalgamation, then the aluminium is rapidly attacked. Aluminium vessels disintegrate quickly if they are amalgamated with even a trace of mercury.

Remove the oil from 2 to 5 g. of aluminium powder by boiling it with a little alcohol; pour off the latter, and cover the aluminium with a $\frac{1}{2}\%$ solution of mercuric chloride. After a few minutes decant off the liquid and wash the powder several times with water. Then cover the amalgamated metal with water and allow it to stand. Within a short time there is an evolution of hydrogen, the mass becomes heated until finally vapors of steam arise, and white hydrated aluminium oxide is formed.

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[1] Cf. No. 13.

[2] Cf. Tables of specific gravity.

It is upon this strong tendency of aluminium to oxidize that the processes of aluminothermy are based.

Mixtures of aluminium and oxides react together energetically, whereby the aluminium is converted into oxide and the metal which originally was in the form of the oxide is set free. Since one gram of aluminium on combustion yields over 7000 calories, almost as much as carbon, and because there are no gaseous products of combustion formed which would carry away heat from the reaction mixture, the temperature is raised to considerably above 2000° C.

A mixture of ferric oxide and aluminium, the "thermite" of commerce, is used for the rapid production of high temperatures in a small space, thus in welding, riveting, etc., by the Goldschmidt process. The aluminium oxide separates out from the reaction in the form of a very hard crystalline substance which can be used as an abrasive; often well-formed needle-like crystals are to be found in the hollow spaces of the slag. Metals like manganese (No. 2), chromium (No. 3), molybdenum (No. 166) and vanadium, which were formerly difficult to prepare, or could at best be obtained only in an unfused state and very impure, can now be prepared without difficulty as fused masses, free from carbon, by the reduction of their oxides with aluminium.

Even silicon and boron can be obtained by an alumino-thermic process, if sulphur as well as an excess of aluminium powder is added to the oxides. The sulphur unites with aluminium and forms a slag of aluminium sulphide, by which reaction the high temperature required for the reduction of the oxides is reached; under the slag a fused mass of metal is formed from which, after dissolving away the excess of aluminium, crystals of silicon, or boron, are obtained. Magnesium, if used in these reactions instead of aluminium, produces similar results.

2. Manganese from Pyrolusite.

The reaction between aluminium powder and pyrolusite is so violent as to be almost explosive; it is better therefore to transform the pyrolusite first into a lower oxide before carrying out the process. Place 500 g. of finely powdered and sifted pyrolusite in a Hessian crucible and heat in a charcoal furnace. Mix the mangano-manganic oxide, Mn_3O_4, thus obtained (about 420 g.), with one-third its weight of aluminium powder.[1] Choose a Hessian crucible, of such a size that it will be about three-fourths filled by the mixture, and embed it in sand in a large, shallow dish. At first add only three or four spoonfuls of the mixture to the crucible; upon the middle of this shake about 2 g. of magnesium powder and in the latter stick a strip of filter paper (10 × 2 cm.) which has been moistened with concentrated potassium nitrate solution and dried. Set fire to the paper by touching it with a torch made by fastening a wad of asbestos to the end of an iron wire, wetting the asbestos with alcohol and setting fire to the alcohol. The torch ignites the paper which has been impregnated with potassium nitrate, the burning paper sets fire to the magnesium and the burning magnesium ignites the thermite mixture. As soon as the reaction has started add the remainder of the charge from an iron spoon, not too much at one time, but still rapidly enough so that the mass in the crucible is kept in a state of brilliant incandescence until the reaction is ended. It is advisable for the operator to wear blue glasses and a heavy glove and the experiment should be performed in a place where no danger can result from flying sparks.

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[1] Use the coarser aluminium powder prepared especially for the thermite process, and not the fine powder employed for aluminium paint.

After cooling, break the crucible and hammer away the slag of fused aluminium oxide from the regulus of metallic manganese. The slag is very hard and will scratch glass. Yield of manganese, about 120 g. Dependent preparation, Potassium Permanganate, Electrolytically No. 84.

3. Chromium from Chromic Oxide.

Chromium cannot be prepared, at least not on a small scale, according to the directions given for manganese, because the heat liberated in the reaction between chromic oxide and aluminium is not sufficient of itself to melt the aluminium oxide. It is, therefore, in this case necessary to heat the crucible and its contents before starting the reaction, or to add to the mixture a little chromate which, by reacting more violently with the aluminium, affords the necessary heat.

1. Mix about 70 g. of chromic oxide (No. 30) with one or two grams less than the calculated amount of aluminium powder; place the mixture in a clay crucible, which should be about two-thirds filled. Add to the above mixture 10 to 15 g. of ignition powder,[1] and place the crucible in a glowing charcoal furnace whereby the ignition powder ignites, and the mass enters into violent reaction. Finally remove the crucible from the furnace, allow it to cool and break it, together with the slag, away from the metallic chromium.

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[1] One part aluminium powder mixed with 10 parts of barium peroxide. Such ignition powder can be purchased all prepared for thermite reactions.

Yield, 30 to 33 g. With smaller amounts of the mixture, a porcelain crucible (which is, however, very liable to break) may be used and heated over the blast lamp.

2. Ignite an intimate mixture of 70 g. ignited chromic oxide, Cr_2O_3, 20 g. of fused and powdered potassium dichromate, $K_2Cr_2O_7$, and 32 g. of aluminium powder *in one portion* with magnesium powder and potassium nitrate paper exactly as described in the preparation of manganese (No. 2). Yield, 30–35 g. of chromium contained in one large regulus and several smaller globules.

Dependent preparation, Anhydrous Chromic Chloride, No. 44.

4. Crystallized Silicon.

Heat some pure, sifted sand in a small evaporating dish until thoroughly dried. Mix together 90 g. of the dried sand, 100 g. of aluminium powder, and 120 g. of flowers of sulphur in a clay crucible which is half filled thereby. Cover the mixture with a little magnesium powder and start the reaction by igniting the latter. The experiment must be performed out of doors, or under a hood with a good draft, as considerable sulphur dioxide is evolved. After cooling, break the crucible and cover the fused pieces with water in a dish also placed under the hood; hydrogen sulphide is set free by the hydrolysis of aluminium sulphide. The aluminium hydroxide and oxide are easily rinsed off from the regulus of metal. Treat the grayish-black, glistening metallic regulus, and any smaller globules of metal that can be extracted, in a beaker with strong hydrochloric acid, keeping it in a warm place for several days and renewing the hydrochloric acid from time to time until finally all of the excess of metallic aluminium has been dissolved away and a loose mass of silicon leaflets remains. Finally boil the crystalline mass with concentrated hydrochloric acid for some time, cool somewhat and transfer to a platinum dish. Add hydrofluoric acid in small portions to react with any silica present. This usually causes considerable evolution of heat. Heat on the water bath for 45 minutes to remove the excess hydrofluoric acid, dilute with water and wash by decantation. Drain the crystals by suction, wash them well with water, and dry in the hot closet. A further treatment of the metal with hydrochloric and hydrofluoric acids should have no effect. Yield, 20 to 25 g. Dependent preparation, No. 51.

5. "Crystallized Boron."[1]

Mix 50 g. of anhydrous boron trioxide, 75 g. of sulphur, and 100 g. of granulated or powdered aluminium in a crucible and bring the charge into reaction in the same manner as in No. 4. After cooling break the crucible and the solidified melt, treat the latter with water and rinse away the aluminium hydroxide, formed by hydrolysis, as well as the microscopic, crystalline needles of aluminium oxide. Pick out the lumps of regulus and free them completely from the last traces of slag both mechanically and by long continued boiling with water. Treat the 30 to 40 g. of purified regulus particles thus obtained with concentrated hydrochloric acid, adding only a little at a time, and after the first violent action is over let stand in a warm place several days until all of the aluminium has dissolved away. A heavy, black, shining mass of crystals is left. Remove the lighter impurities by repeated decantation with water; boil with concentrated hydrochloric acid, placing a round flask filled with cold water over the beaker in order to condense the acid vapors; then warm with hydrofluoric acid in a platinum dish for several hours, wash again, and finally allow to stand in a warm place with dilute hydrochloric acid until no more bubbles of gas are given off. The last traces of aluminium dissolve very slowly.

About 7.5 g. of small, compact, mostly opaque, black crystals are obtained which have a luster resembling that of hematite. The thinnest crystals, which are most often six-sided, show a deep dark-red color by transmitted light. The crystals scratch glass. They were formerly taken to be pure crystallized boron; their composition, however, corresponds to the formula AlB_{12}.

REDUCTION WITH POTASSIUM CYANIDE.

6. Tin from Cassiterite; Melting-point Determination.

Native stannic oxide, SnO_2, in spite of the fact that tin is closely related to the noble metals, can be reduced by carbon only at a very high heat. The reduction takes place far more readily with potassium cyanide, the latter being oxidized thereby to potassium cyanate:[2]

$$KCN + O = KCNO.$$

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[1] H. Biltz, Ber. **41**, 2634 (1908). According to the advice of Dr. K. Schaefer it is well to add a little ignition mixture (barium peroxide and aluminium) to the charge.

[2] Some samples of cassiterite are not reduced readily.

This method, on account of the relatively high cost of potassium cyanide, is used only in the laboratory or in the technical reduction of very valuable metals from their oxides.

Heat a mixture of 20 g. of very finely-powdered cassiterite and 20 g. of potassium cyanide in a porcelain crucible, which should be about three-quarters filled thereby, for half an hour over the blast lamp. A clay mantle may be placed around the crucible to lessen the amount of heat lost by radiation. After cooling, wash the regulus of metallic tin (12 to 15 g.) with water. Express the yield in per cent of the weight of mineral taken. Test the tin qualitatively for iron, copper, and lead, and determine its specific gravity. The specific gravity of pure tin (in the white modification) is 7.287 at 15°.

Melting-point Determination.

The difference in the energy content of a substance in different states of aggregation is a far more distinctive property than the mere outward characteristics, — solid, liquid, and gaseous. Such energy differences can be measured in the heat of fusion or of vaporization.

The melting-point of a substance can, therefore, be determined very accurately if it is uniformly heated and the changes of temperature, as shown by an inserted thermometer, are observed. As soon as the melting-point is reached, the mercury remains stationary until all of the metal is melted even although the outer temperature is higher; the heat supplied to the substance is all utilized in causing its fusion before any is available for producing a further rise of temperature. If the outer temperature is only a few degrees higher than the melting-point, the temperature of the substance remains constant for a considerable time, so that the thermometer may be read accurately. On cooling a fused substance, the thermometer likewise remains constant for some time at the solidification point, even when the outer temperature is lower. With pure substances the melting-point and the solidification-point are identical.

Cut the tin into a few small pieces and place it in a test tube of 1 cm. diameter which dips 4 cm. into a small beaker filled with sulphuric acid. Cover the beaker with a disk of asbestos board provided with a hole into which the test tube fits. Heat the sulphuric acid until the tin just melts; then heat a thermometer cautiously over a flame to about 200° and dip it into the molten metal. Lower the flame under the beaker so that the temperature of the bath falls slowly, and, while stirring, observe the changes of the thermometer reading. At the solidification point the temperature remains constant for from 10 to 20 minutes. In determining this temperature, a *supercooling* occurs regularly; i.e., the thermometer at first falls a few degrees below the solidification point while the mass still remains perfectly liquid. Then, as the crystals of the solid begin to separate, the temperature rises rapidly to the solidification point, where it remains perfectly stationary while the mass is crystallizing. After this point is determined, increase the flame a little and find the melting-point in an exactly corresponding manner. Tin melts at 232° C.

In using a long, ordinary thermometer the observed temperature is always a few degrees too low because the entire thread of mercury is not at the desired temperature. Such an observed reading gives the "uncorrected melting-point." It may be corrected by adding the value, $0.000{,}16 \cdot \alpha\ (t - t_0)$, in which α is the length in scale degrees of the exposed thread of mercury, t is the observed reading, and t_0 the average temperature of the exposed mercury. This last value is obtained by a second thermometer, the bulb of which is placed at about the middle of the exposed mercury column. The correction is usually spoken of as the "correction for stem exposure." Another method for applying the correction for stem exposure has been proposed by E. Rimbach;[1] see also Preparation No. 49.

7. Pure Antimony from Basic Antimony Chloride.

Basic antimony chloride (antimony oxychloride) is a by-product in the preparation of antimony trichloride (No. 47). Grind the dry basic chloride with twice its weight of powdered potassium cyanide, and heat the mixture in a porcelain crucible over the blast lamp. To prevent loss of heat by radiation, surround the crucible with a piece of iron stovepipe, a flowerpot, or a larger graphite crucible, the bottom of which is cut off. After cooling wash the metallic regulus with water until all the adhering slag is removed. The antimony has a silver-white appearance and shows a crystalline structure.

Regarding the density of antimony, see page 16. Dependent preparation, No. 88.

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[1] Ber. **22**, 3072 (1889).

REDUCTION WITH AQUEOUS REDUCING AGENTS.

8. Selenium Dioxide and Pure Selenium from Crude Selenium.

From a dilute aqueous solution of selenious acid, the element selenium is precipitated by soluble reducing agents, such as sulphurous acid or hydrazine salts:

$$SeO_2 + 2\ H_2SO_3 = 2\ H_2SO_4 + Se.$$

A suitable solution of selenious acid may be obtained by oxidizing the raw material with nitric acid; selen*ic* acid is not formed under these conditions (difference from sulphur).

Place 20 g. of crude selenium in an evaporating dish, and after covering the dish with an inverted funnel, oxidize by the gradual addition of 50 g. of concentrated nitric acid. Evaporate the solution upon the water bath; and after drying the residue at 110° to 130°, sublime it from wide test-tubes, or from an evaporating dish, into a large inverted beaker. The sublimate is usually somewhat reddish in color, due to the presence of a small amount of elementary selenium; therefore treat it once more with nitric acid, evaporate the solution to dryness, and take up the residue in water. Reduce the selenious acid, at the room temperature, by passing into the solution sulphur dioxide gas which has been washed with water. A red precipitate of selenium is slowly formed; the precipitation takes place more rapidly, however, in the presence of a little hydrochloric acid. The red, amorphous product can be dried *in vacuo* over sulphuric acid without change, but by warming it in contact with the solution from which it has been precipitated, it goes over into gray selenium.[1]

Selenium imparts a blue tinge to the Bunsen flame. A porcelain dish held in this flame becomes coated with a brick-red (reduction) spot which is surrounded by a white (oxidation) ring. At the same time a characteristic, radish-like odor is noticed, which can be obtained even more distinctly by heating selenium on charcoal before the blowpipe.

9. Extraction of Gold.

Gold can be obtained mechanically by "panning" the stamped, or ground ore, or, more advantageously, by treating the powdered ore with mercury which dissolves out the gold. Ores with a small gold content, and those in which the gold is chemically united with some other element, are treated either with chlorine water, whereby chlorauric acid $H[AuCl_4]$ is formed, or with potassium cyanide solution, which, together with atmospheric oxygen, converts the gold into potassium aurocyanide, $K[Au(CN)_2]$.

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[1] Vessels stained with selenium can be cleaned with potassium cyanide solution, whereby readily soluble KCNSe is formed.

For the following experiments, employ a sand that is very poor in gold; in case such is not at hand, mix sand with a little high-grade gold ore, or moisten the sand with a gold solution and dry it by ignition.

Kröhncke's Method of Preparing the Gold Solution. Mix 10 to 100 g. of ore intimately with one-fourth its weight of sodium chloride (to form $NaAgCl_2$ with the silver present) and a little potassium chlorate; moisten the mixture well with concentrated hydrochloric acid in a small flask, and allow it to stand for 12 to 24 hours at the room temperature with occasional shaking. Then heat it on the water bath until the greater part of the free chlorine has been expelled. Finally, dilute with water, whereby any silver chloride is precipitated, and filter. Evaporate the filtrate to a small volume on the water bath, and carry out with this solution the two reactions given below.

Döring's Method of Preparing the Gold Solution. Place the sample of ore in a glass-stoppered flask, add 1 cc. of bromine and about the same amount of ether, and shake frequently. After two hours — vapors of bromine must still be visible — add 50 c.c. of water and allow the mixture to stand another two hours in a warm place. Filter the solution and evaporate it to one-fourth of its former volume.

Tests. To detect the presence of gold in either of the above solutions, treat one part with freshly-prepared ferrous sulphate solution, whereupon the liquid first assumes a reddish-violet coloration, and then becomes turbid through separation of gold. With the solution prepared by the Kröhncke method a considerable quantity of the ferrous sulphate should be used. Treat a second portion of the solution with a few drops of bromine water and a little stannous chloride solution, whereby the solution becomes colored at first blue, then brownish violet, and later red; in this test an adsorption compound of gold and stannic hydroxide is formed (Purple of Cassius); cf. No. 25.

According to the above directions, the presence of about 0.05 mg. of gold in the ore can be detected.

DESULPHURIZATION OF SULPHIDES BY THE PRECIPITATION PROCESS.

10. Antimony from Stibnite.

Sulphides containing lead and antimony are frequently treated metallurgically by the so-called "Precipitation Process." By this is understood the fusion of the ore with iron and suitable substances to form a slag, whereby the iron serves as a desulphurizing agent. The sulphide of iron formed dissolves in the slag, and the precipitated metals collect at the bottom of the furnace.

Place a mixture of 100 g. powdered stibnite, 42 g. iron filings, 10 g. anhydrous sodium sulphate, and 2 g. wood-charcoal powder in a Hessian crucible and heat in a charcoal furnace. The temperature should not rise high enough to melt the iron sulphide slag completely, but just sufficiently to soften it; this point is determined by stirring the fusion with an iron rod. After cooling and breaking the crucible a fused mass of antimony, weighing about 65 g., is found at the bottom. Test a sample of this crude antimony qualitatively for the presence of arsenic, copper, iron, and lead.

Purification I. Mix the finely-powdered, crude antimony with one-fourth its weight of powdered stibnite and an equal amount of anhydrous sodium carbonate, and melt over the blast lamp in a porcelain crucible surrounded with a clay mantle. Yield, 60 to 65 g.

Purification II. To remove arsenic from the antimony purified according to I, pulverize the metal again, mix it with 4 g. sodium carbonate and 0.2 g. potassium nitrate, and melt the mixture in the manner just described. Yield, 50 to 55 g. of pure antimony. Dependent experiment, No. 88.

11. Mercury from Cinnabar; Sodium and Ammonium Amalgams.

✓ 23, HgS 5 gr Fe

Heat a mixture of 23 g. cinnabar and somewhat more than the calculated amount of iron filings in a small retort of difficultly-fusible glass. The mercury distils into a small flask which serves as receiver. Yield, 16 to 18 g.

✓ *Sodium Amalgam.* Pour the mercury so obtained into a test tube and add clean, freshly cut pieces of sodium, about the size of grains of wheat, waiting each time before adding a fresh piece until the previous one has reacted; toward the end assist the reaction by heating. Use 1 g. of sodium in all. After cooling, break the test tube and collect the amalgam, which will keep indefinitely when preserved in well-stoppered vessels. A lump of sodium amalgam placed in water gives a uniform evolution of hydrogen.

Ammonium Amalgam. Introduce a few grams of sodium amalgam into 20 to 30 c.c. of ice-cold, concentrated ammonium chloride solution; the amalgam at once begins to swell, and is changed to a gray spongy mass of extremely voluminous ammonium amalgam. Ammonium amalgam decomposes completely, within a short time, into hydrogen, ammonia, and mercury.

ROASTING PROCESSES.

12. Lead from Galena.

By the "roasting process" galena is first partly oxidized at a relatively low temperature to lead oxide or lead sulphate; then without any introduction of air the mass is heated more strongly, whereby the oxygen of the lead oxide and lead sulphate accomplishes the oxidation of all the sulphur present to sulphur dioxide. Only those ores are suitable for roasting which contain but small amounts of silicates and of sulphides of other metals. Silicates are harmful, since they give rise to the formation of lead silicate. As it is difficult to conduct the partial roasting satisfactorily upon a small scale, it is better in the following experiment to start with a mixture of galena and litharge:

$$PbS + 2\ PbO = 3\ Pb + SO_2,$$
$$PbS + PbSO_4 = 2\ Pb + 2\ SO_2.$$

Place an intimate mixture of 20 g. very finely-powdered and sifted galena and 37 g. litharge in a small clay crucible, and heat it in a furnace as quickly as possible to a bright red heat. After about half an hour, allow the contents of the crucible to cool, and hammer away the regulus of metallic lead from the broken crucible to which it adheres because of a glassy film of lead silicate. To purify the lead, melt it together with some borax in a porcelain crucible. Calculate the yield in per cent of the theoretical.

CUPELLATION.

13. Pure Silver from Coin Metal.

If an alloy of impure precious metal, such as gold, silver or platinum, is melted on a cupel in an oxidizing atmosphere, the lead and other base metals present are oxidized and are absorbed by the porous material of which the cupel is made. This process is made use of technically for obtaining pure silver from the impure metal, and for working up argentiferous lead which is obtained in the metallurgy of certain lead ores; the process is likewise used on a small scale in the rapid and accurate quantitative estimation of silver and gold in ores or metallurgical products (fire-assay).

Melt together, by means of a slightly luminous flame from a blast lamp, about 0.3 g. of silver coin and 1 g. of pure lead in a flat cavity, made as smooth as possible, in a piece of blowpipe charcoal. Press some bone-ash firmly into a small porcelain crucible with a pestle so that at the top there is a slight hollow with a coherent, perfectly smooth surface. Place the metallic button by means of pincers upon the bone-ash which is to serve as a cupel. Support the porcelain crucible on a clay triangle, or embed it in sand, with its top slightly inclined towards the blast lamp; and direct the point of the oxidizing flame toward the vicinity of the button, and some of the time directly upon it. At first keep the metal but barely melted, as otherwise it is likely to spirt. The lead oxide, as fast as it is formed, runs off and is absorbed by the bone-ash; in order that it may not all run into the same place change the inclination of the crucible from time to time. Continue the heating until the size of the button no longer diminishes; towards the end apply a higher heat, whereby films of metallic oxide run across the button in the direction of the oxidizing draft, and lead oxide separates out on the opposite side in the form of dark-brown crystals containing copper. The end of the process is reached upon the disappearance of the oxide film, which at the last shows for an instant a rainbow-like play of colors. This is known as the "blick." After this point is reached, further heating causes a loss of silver by volatilization. During the process a part of the lead is volatilized.

The metal still contains a small amount of copper. Melt it again with 1 g. lead, and cupel the greater part of this lead away as before, using a fresh cupel. Free the button from bone-ash by hammering it into a cube (holding it in pincers), and remove the last traces of lead by heating it on a third cupel. Weigh the silver button that is finally obtained. Yield, 96 to 97% of the actual silver content of the coin.

METALS BY ELECTROLYSIS.

14. Lithium from Fused Lithium Chloride.

Fused lithium chloride, like the aqueous solution of this salt, is largely ionized and consequently can act as an electrolyte. According to the present theory, the passage of an electric current represents a movement of tiny particles of negative electricity called *electrons* (cf. p. 9). If an electric current passes through an electrolyte there is always chemical decomposition at each electrode, an oxidation at the anode and a reduction at the cathode. Thus the electrolysis of fused lithium chloride results in the simultaneous formation of metallic lithium at the cathode and chlorine gas at the anode. At the cathode, where the negatively-charged electrons pass from the wire to the electrolyte, the positively-charged lithium ions are neutralized and neutral, or free, lithium is formed. At the anode, where electrons leave the fused salt and pass to the anode and thence to the conducting wire, each negatively-charged chloride ion gives up one electron and neutral, or free, chlorine results. These reactions of reduction (lithium) and oxidation (chlorine) can be expressed by the following equations in which the symbol ϵ is used to represent the electron, or unit charge of negative electricity

$$2\,\mathrm{Li}^+ + 2\,\epsilon = 2\,\mathrm{Li} \qquad 2\,\mathrm{Cl}^- = \mathrm{Cl}_2 + 2\,\epsilon.$$

The electron, therefore, represents one unit negative charge, such as is represented by the negative charge on one atom of chlorine in the chloride ion. Although it seems probable from the results of several methods of experimentation that there are about 6.1×10^{23} atoms of lithium in one gram atom, so that we have a fairly good idea as to the actual magnitude of the unit charge of electricity, it is more advantageous to think in terms of the gram atom which, in the case of lithium or any other univalent ion, bears a charge of 6.1×10^{23} units of electricity. This larger value corresponds to 96,500 coulombs or 26.82 ampere hours and represents the quantity of electricity required to set free 6.940 grams of lithium and 35.46 grams of chlorine when all of the electrical current passing through fused lithium chloride is utilized for producing lithium at the cathode and chlorine at the anode. Thus, with 100% current yield, a current of one ampere passing through lithium chloride for one hour (3600 seconds) will set free $\frac{6.940 \times 3600}{96{,}500} = 0.2589$ g. of lithium and $\frac{35.46 \times 3600}{96{,}500} = 1.322$ g. of chlorine. Or, since at 0° and 760 mm. pressure, one molecule of chlorine or any other gas occupies a volume of about 22.4 liters, one can say that 96,500 coulombs will liberate 11.2 liters of chlorine gas. This quantity of electricity, 96,500 coulombs, is called one *Faraday*, because Michael Faraday recognized about the year 1835 that the quantities of different elements liberated by a given quantity of electricity were proportional to the atomic weights, or simple multiples of the atomic weights, of the elements (Faraday's law).

In carrying out electrolytic preparations, the apparatus is usually arranged in accordance with the following scheme (Fig. 9), which is, in principle, identical with that employed in electro-analysis. The decomposition cell, an ammeter, and a regulating-resistance are introduced in series into an electric circuit. The binding clamps of the cell may also be connected with wires from a voltmeter in order to determine the difference in potential between the two poles during the electrolysis. The ammeter should remain in the circuit throughout the whole of the electrolysis; the voltage is measured only from time to time, and has less value for determining the course of the reaction when one is working according to well-tested directions. A storage battery may serve as the source of electricity; for measuring the current and voltage the simpler and inexpensive instruments suffice, and their reliability can be determined easily by comparison with standard instruments.

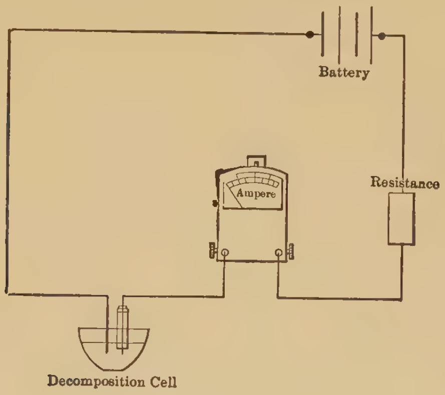

Fig. 9.

In all cases where a metal which decomposes water is to be prepared, a fused compound rather than its aqueous solution must be used for the electrolyte. The melting-point of the salt may be lowered by admixture with some other suitable salt.

Mix together 30 g. of dry lithium chloride and an equal weight of dry potassium chloride in a porcelain crucible, 6 to 8 cm. high and 9 cm. in diameter. Melt the mixture and then after starting the electrolysis maintain a sufficient flame to supplement the heating effect of the current in keeping the mass just liquid. For the anode, use a rod, 0.8 cm. in diameter, of arc-lamp carbon which is not attacked by the liberated chlorine; and for the cathode use an iron rod 0.3 cm. thick. Insert the cathode through a cork in the upper end of a glass tube, of 2 cm. diameter, and place the whole in the fused electrolyte so that the glass tube dips 1 cm. below the surface and the iron rod 0.3 cm. deeper (Fig. 9). The metallic lithium collects in the space between the iron wire and the glass tube, and the glass mantle protects it from being disseminated throughout the electrolyte. When all is ready close the circuit, noting the time, and regulate the resistance so that a current of between 6 and 10 amperes passes. In order to obtain this current, the voltage of the storage battery, since it has the resistance of the electrolyte to overcome, must not be too small; it should be between 7 and 12 volts (3 to 6 accumulator cells connected in series). During the electrolysis note frequently the time and amperage, and from these readings compute the number of ampere-seconds by multiplying the average reading of the ammeter by the number of seconds which have elapsed.

When the reaction is progressing with moderate strength, but without being disturbed by too vigorous an evolution of chlorine, metallic lithium can be observed collecting at the cathode in the space between the iron rod and the glass tube. From time to time flashes of light occur at the anode which are probably due to an insulating envelope of chlorine gas which is formed about the carbon and causes a marked lessening of the current; this difficulty is easily remedied by occasionally breaking the circuit for a moment. At the end of twenty minutes a considerable amount of lithium should have collected. Raise the cathode from the fused salt, holding an iron spoon to prevent any lithium from falling out of the glass tube, and dip the whole under petroleum. After cooling remove the lithium from the tube with a knife and weigh it under petroleum. The current yield, i.e., the yield reckoned on the amount which the current should theoretically produce, is about 70%.

The lithium thus prepared is contaminated with a little potassium. Determine the density by means of a pycnometer, using petroleum of known density. For this purpose weigh the pycnometer (1) empty, (2) filled with petroleum, (3) containing the lithium alone, and (4) containing the lithium and enough petroleum to fill the instrument completely. From these weighings and the known density of the petroleum, the density of the lithium can be computed; it should be 0.534.

CHAPTER II.

CHANGES OF CONDITION.

Changes in the state of aggregation of substances have already been mentioned in the preceding chapter; but under changes in condition are included also polymerization and dissociation, as well as the formation of allotropic, passive, amorphous, and colloidal modifications. These phenomena are, with few exceptions, not confined to any particular class of substances.

POLYMERIZATION AND DISSOCIATION.

The phenomena of polymerization and dissociation, as far as they occur with gaseous or dissolved bodies, are capable of a complete theoretical interpretation. By polymerization is understood the adding together of particles of material of the same kind to form larger aggregates; the opposite of this process is dissociation. The occurrence of either may be demonstrated by determining the molecular weight of the substance in the vaporized or dissolved state. For example, the diatomic iodine molecules dissociate at high temperatures into atoms; on cooling, the atoms again polymerize into molecules of the original sort:

$$\underset{\text{Polymerization}}{\underset{\longleftarrow}{\overset{\text{Dissociation}}{\overset{\longrightarrow}{I_2 = 2\,I}}}}$$

In a similar way ferric chloride forms simple molecules at high temperatures, and double molecules at lower temperatures:

$$\underset{\text{Polymerization}}{\underset{\longleftarrow}{\overset{\text{Dissociation}}{\overset{\longrightarrow}{Fe_2Cl_6 = 2\,FeCl_3}}}}$$

The enumeration of experiments illustrating these phenomena may be dispensed with at this point; the conception of dissociation, however, is developed more fully in the general section of Chapter III, and that of electrolytic dissociation in the sections on acids, bases, and salts, and in No. 34.

ALLOTROPY.[1]

Many solid substances appear, under different conditions, in two or more distinct forms (known as allotropic modifications), which are distinguished from one another by color, density, crystalline form, solubility, and other physical properties. The best known instances of this are shown by carbon and phosphorus.

In the same way that different states of aggregation are separated by a temperature boundary which is dependent on the pressure, so also for the mutual transformation of numerous allotropic forms, there is a definite temperature, dependent only on the pressure, below which the one, above which the other form is stable. This is known as the transition temperature.

In addition to this sort of allotropy, which, because the two forms can change simultaneously into one another and can exist in equilibrium at the transition temperature, is known as *enantiotropy*, there is also a second sort known as *monotropy*. Two modifications of a substance are monotropic when the one changes into the other, but the latter cannot change back directly into the first. They possess no transition temperature; one form is under all conditions less stable than the other, and therefore is only to be observed in virtue of the extreme slowness with which the transformation takes place.

An example of enantiotropy is shown by sulphur, which above 96° is monoclinic, below 96° rhombic. An example of monotropy is furnished by iodine chloride, ICl, the labile form of which melts at 14° and the stable form at 27°. (Cf. No. 55.)

The energy difference between allotropic modifications corresponds entirely with that existing between the solid and the liquid states and, like the latter, is measured by the heat of transformation.

For determining the transition point of allotropic forms, the following methods are chiefly used:

(1) The Thermic Method. The point on the heating or cooling curve is determined at which, in consequence of the absorption or setting free of the heat of transition, a retardation in the otherwise steady rise or fall of temperature occurs; compare the determination of the melting-point of tin, No. 6, also Nos. 15 and 16.

(2) The Dilatometric Method, which depends on a comparison of the densities (or of the volumes) on both sides of the transition point.

(3) The Optical Methods, which frequently permit a very sharp observation of a change in crystalline form, or in color, at the transition point. (No. 17.)

(4) Electrical Methods. (a) The electrical conductivity of a substance is plotted graphically against the temperature and the point of inflection of the curve determined.

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[1] Concerning allotropy, see also B. Roozeboom, Heterogene Gleichgewichte, Vol. 1, p. 109 (1901).

(b) The temperature is found at which the difference of potential between each of the two modifications and some common electrolyte is the same; in other words, the electromotive force of an element constructed from the two modifications and a common electrolyte is equal to zero.

15. Allotropy of Silver Sulphide.

Silver sulphide has a transition temperature of above 170°, which can be determined both from the electrical resistance and from the cooling curve. The phenomenon of supercooling not being very pronounced with this substance, a point of inflection is found on the cooling as well as on the heating curve; on the former it lies naturally at a lower temperature than on the latter.

In order to prepare silver sulphide, treat a hot solution of about 20 g. of silver nitrate in 300 to 400 c.c. of water with hydrogen sulphide, and wash the precipitate by decantation. After removing the liquid by suction, dry the preparation in the hot closet. Silver sulphide thus formed is not absolutely free from uncombined sulphur.

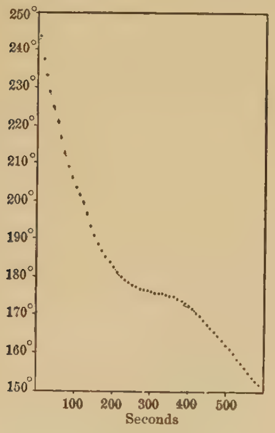

Fig. 10. Cooling Curve.

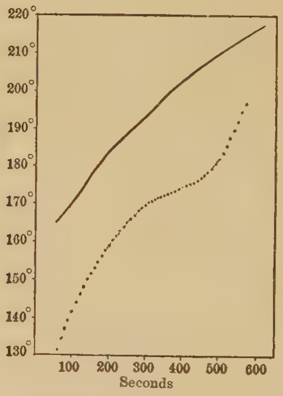

Fig. 11. Heating Curve.

Place about 8 g. of the silver sulphide in a test tube and insert a thermometer. Heat the test tube to about 290° in an air bath, consisting of a porcelain crucible covered with a piece of asbestos board. Some sulphur sublimes, but this does not interfere with the experiment. Then transfer the test tube quickly to a small beaker containing sulphuric acid or paraffin at 145°, which temperature must be kept constant to within a few degrees throughout the experiment. Read the temperature every 10 seconds and plot the results (Fig. 10).

When the temperature has fallen to about 130°, proceed to obtain the heating curve by warming the bath so that its temperature keeps constantly 20° or 30° above that of the sulphide (Fig. 11); the continuous curve gives the bath temperatures, the dotted one the readings for the silver sulphide. The point at which the transformation is finished, and the temperature begins to rise rapidly is particularly sharp.

16. Allotropic Modifications of Sulphur.

Monoclinic sulphur has a density of 1.96 and a melting-point of 119.25°; rhombic sulphur a density of 2.06 and a melting-point of 112.8°. When sulphur crystallizes from a solution in carbon bisulphide, it is obtained in the rhombic modification, which at room temperature can be preserved unchanged for an indefinite time. If on the other hand melted sulphur is allowed to solidify, the crystals which form are not of the rhombic, but are commonly of the monoclinic, modification; this modification persists for some time, even below the transition temperature, as an unstable form, for the reason that the transition takes place slowly. In addition there have been six or seven other allotropic forms of sulphur shown to exist by crystallographic optical methods.

Monoclinic Sulphur. Transformation into Rhombic Sulphur. Heat about 7 g. of sulphur in a test tube until it has melted and begun to turn dark-colored (140° to 150°); dip a thermometer in the liquid and clamp it in position. Allow the melted sulphur to cool in a sulphuric-acid bath at 80° to 90°, and when it is at 110° arrest the supercooling by dipping a glass thread into the melt. The sulphur crystallizes to a wax-yellow mass of transparent monoclinic needles, while the liberated heat of solidification raises the temperature several degrees. By the next day, or more quickly on moistening the mass with carbon disulphide, the crystals become light-yellow and opaque, changing thereby into an aggregate of rhombic crystals.

Transformation of Rhombic into Monoclinic Sulphur. Heat a few clear crystals of rhombic sulphur for two or three hours in a test tube which dips in a bath of a boiling, concentrated solution of common salt (temperature 108° to 112°), replacing when necessary the water evaporated from the bath. The sulphur crystals gradually become clouded, and change finally to a friable, light-yellow mass of monoclinic sulphur.

The Transition Temperature from the Heating Curve. The cooling curve of sulphur does not, when determined in the simplest manner, show an exact point of solidification, because this is dependent on the temperature to which the material has previously been heated; nor does it indicate sharply the transition temperature, on account of the ability already mentioned of monoclinic sulphur to persist in the unstable condition. Both values, however, can be established within 5° if the rate is measured at which the temperature of rhombic sulphur rises with a uniform application of heat.

Melt about 7 g. of sulphur in a test tube, place the bulb of a thermometer in the liquid, let the latter solidify, and after moistening it with a little carbon bisulphide allow it to stand until the next day. It is well also to prepare one or two duplicate tubes in the same manner. Heat one of the tubes in a sulphuric-acid bath in such a manner that the temperature of the bath keeps constantly about 15° in advance of that shown by the thermometer in the tube, and never rises more rapidly than 1° in 10 seconds. Read the thermometer every 10 seconds between 60° and 120°, and plot the corresponding temperatures and times on coördinate paper. The rise in temperature is retarded between 95° and 100° (the transition point) in consequence of the amount of heat absorbed in the transformation. In the further course of the curve there is only a moderately rapid rise in temperature, — partly because the transition is not completed, partly because melting begins — until, above a point between 115° and 120° (the melting-point), the temperature again rises rapidly.

Allow the melt to cool again, and induce crystallization between 110° and 100° by means of a glass thread, or by seeding with a minute monoclinic crystal; then allow to cool further to 60°, and repeat the experiment. This time, since only monoclinic sulphur is present, there is no indication of a transition point; the melting-point, however, is shown, although, as in the preceding experiment, it is not sharply defined.

According to recent investigations, it seems probable that the peculiar changes in consistency and color which sulphur undergoes on further heating are due to two different liquid modifications: $s\lambda$ the thin liquid and $s\mu$ the viscous form.[1]

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[1] Smith and Holmes, Z. physik. Chem. **42**, 469 (1903); **52**, 602 (1905);

When sulphur is heated in a test tube above 160° it becomes dark and so viscous that the tube can be inverted without the sulphur flowing out.

17. Transition Point of Cuprous Mercuriiodide $Cu_2[HgI_4]$ and of Silver Mercuriiodide $Ag_2[HgI_4]$.

First prepare mercuric iodide by precipitating a solution of 6.8 g. of mercuric chloride with a solution of 8.3 g. of potassium iodide. Wash the precipitate once by decantation, and dissolve it together with 8.3 g. of potassium iodide in 50 c.c. of water. Mix the filtered solution with another filtered, concentrated solution containing 12 g. of blue vitriol, and pass sulphur dioxide into the filtrate, in order to reduce the cupric salt. The sulphur dioxide can be prepared from sodium sulphite and sulphuric acid (cf. footnote, page 71). A bright-red precipitate is produced of somewhat the appearance of mercuric iodide. Wash it thoroughly on the suction filter and dry it in the hot closet. Yield, about 20 g.

Cuprous mercuriiodide is transformed at about 71° into a black modification. The color change can be observed if a pinch of the material is gently heated in a test tube over a free flame; on cooling, the black color changes again to red. To determine the transition temperature, a sample may be heated slowly in a dry test tube which is immersed in a beaker of water containing a thermometer that serves also as a stirrer. By means of several repetitions, the transition temperature may be obtained in this way with considerable accuracy.

The silver salt also of hydromercuriiodic acid, $H_2[HgI_4]$, possesses a transition point between 40° and 50°, which is likewise characterized by a change in color. Below this temperature the salt is yellow; above, it is red.

Precipitate a few cubic centimeters of mercuric chloride solution with a solution of potassium iodide, and redissolve the precipitate in an excess of the precipitant. Then add a few drops of silver nitrate solution and observe, without filtering, the change in color of the precipitate on heating and cooling. This transition point is less sharp than that of the copper salt.

54, 257 (1906). Hoffmann and Rothe, *ibid.* **55**, 113 (1906); Smith and Carson, *ibid.* **63**, 273 (1908). With respect to the influence of different forms of S on the melting point, see Beckmann, Paul, and Liesch, Z. anorg. Chem. **103**, 189 (1917).

THE PASSIVE CONDITION.

The change of some metals, particularly chromium and iron, into the passive condition is a phenomenon distinct from allotropy, and one of which the significance is not yet fully understood. The surface of metals when passive is more "noble" than when they exist in the ordinary state, as is shown by the lesser tendency to react chemically, and by the electrochemical behavior; in other respects there is no distinction between the ordinary and the passive conditions.

Metals can be obtained in the passive state by treatment with nitric acid, or other oxidizing agents, or by anodic oxidation.

18. Passive Iron.

Fill a small beaker with concentrated nitric acid, a large one with water, and another small one with copper sulphate solution. Suspend a piece of iron 4 to 5 cm. long (a thick iron screw will answer) bv a platinum wire and submerge it completely in the nitric acid, then lift it cautiously from the acid, rinse it in the water, and finally dip it into the copper sulphate solution, using care in each operation not to allow the iron to come in contact with any solid object, nor to suffer any jar. When the iron is taken from the copper sulphate solution it shows a gray color; it has not reacted with the copper salt. The reaction takes place immediately, however, when the passive condition is destroyed; for example, by striking a sharp blow with a glass rod. Starting from the point hit, a coating of copper, which precipitates from the adhering film of copper salt solution, spreads over the surface of the iron.

The experiment can be repeated immediately, for the coating of copper is quickly dissolved in the nitric acid. When carried out on a larger scale this experiment is well adapted for lecture demonstration.

AMORPHOUS STATE.

As already stated, the phenomenon of supercooling is very generally observed when melted substances solidify. This can often be obviated by means of "seeding" with small fragments of the crystallized substance. In other cases the supercooling persists far below the true temperature of crystallization, and a gradual changing into the crystalline form takes place only very slowly, or perhaps not even to a detectable extent. Such strongly supercooled fluids are designated as amorphous substances when they, like glass or obsidian, possess such a viscosity that they appear to be solid bodies. The amorphous solid condition is, therefore, not distinguished from the fluid state by any discontinuity, but is so distinguished from the solid crystalline condition. It is possible by certain expedients, for example by continued heating at just below the melting-point, to hasten the rate of crystallization, as in the devitrification of glass. With substances which are capable of solidifying in either a crystalline or amorphous condition, the quantity of crystals obtained is for this reason greater, the more slowly the cooling takes place.

19. Amorphous Sulphur.

Distil 40 g. of sulphur from the bulb of a small retort and allow half, as it condenses in the neck, to flow into a mixture of ice and water, the other half into boiling water. Dry these two preparations externally with filter paper, then leave them for several hours at 50° to 60° to dry still further. The next day extract 5 to 10 g. of each of the samples with carbon bisulphide in a Soxhlet apparatus, using a weighed extraction-thimble. Determine, by weighing again, the percentage of each sample of sulphur which has been dissolved in the carbon bisulphide. The sample which was slowly cooled dissolves almost completely, since it has changed into the soluble rhombic form; the suddenly cooled sample leaves behind 30 to 50% of amorphous, insoluble sulphur.

If a mixture of sulphur and ammonium carbonate is distilled, and the sulphur, as in the first case above, is cooled suddenly in the freezing mixture, a product is obtained which contains 90% of the soluble rhombic form, since the presence of ammonia accelerates catalytically the transformation.

COLLOIDAL STATE.

A large number of substances are capable of apparently dissolving in water to form what may be termed pseudo-solutions; such pseudo-solutions are characterized by an extremely small diffusive power, a low osmotic pressure, and an inability to undergo dialysis; in these respects they differ from true solutions of crystalloids, and are thus called *colloidal solutions* (Graham, 1862). Colloidal solutions are distinguished, according to the nature of the solvent, as *hydrosols*, *alcosols*, etc. If the dissolved, or, more correctly, the *pseudo-dissolved* substance is separated from the solvent, it is often found not to have lost the power of again passing into colloidal solution (reversible colloids). On the other hand, there are numerous substances, particularly inorganic ones, which are unable of themselves to pass directly into colloidal solution, but can by suitable means be brought into that state; if such substances are separated from the solution, they do not possess the power of dissolving again unaided (irreversible colloidals).

Solutions of irreversible colloids can be obtained by disintegrating the substance in the electric arc under water (Bredig's method; see No. 20), by forming the substance in aqueous solution by double decomposition and preventing its precipitation by suitable means (Nos. 21; 24, Note on zircon oxide hydrosol; No. 25), or by previously imparting to the solid the ability to dissolve by treatment with small quantities of alkali or acid. The last method was compared by Graham with the process of digestion and called by him *peptonization* (No. 25, tin-oxide hydrosol).

By means of optical methods (ultramicroscopic investigation), it has been proved that many of these colloidal solutions consist really of suspensions of extremely small particles the size of which can be estimated down to a diameter of about 6 $\mu\mu$. In this manner the formerly-very-puzzling fact of the existence of solutions of substances that are ordinarily insoluble, such as gold, platinum, and the sulphides of the heavy metals, finds its explanation.

Modern views concerning the nature of colloids indicate that any substance under proper conditions can be obtained in the colloidal state. There is no sharp distinction between *mechanical suspensions* of a finely powdered substance in a liquid, a *colloidal solution* and a *true solution*. It seems to be merely a matter of size of the individual particles of the substance. By employing micro-photographic methods and working with the short waves of ultra-violet light, the limit of microscopic vision with an ordinary microscope is reached at diameters of about 0.001 mm. or 1 micron (symbol μ). The pores of the best grades of hardened filter paper are about 1 μ in diameter. Clay and porcelain filters have pores about 0.2–0.4 μ in diameter. The size of the average molecule varies from 0.0001 to 0.001 μ or, using the term *micro-micron* or *amicron* to represent one-millionth of a millimeter (symbol $\mu\mu$), the diameter is 0.1–1 $\mu\mu$. A very large molecule such as starch has a diameter of about 5 $\mu\mu$.

On the basis of the size of the particles which a powdered substance assumes when it is shaken with a liquid, it is possible to distinguish arbitrarily between suspensions, colloidal solutions and true solutions. If the particles have diameters of 0.1 μ or more, so that they may be removed by filtration and can be seen under the microscope, the solid substance is said to be *in suspension*. If the diameters of the particles of solid lie between 0.1 μ and 1 $\mu\mu$, the mixture of solid and liquid is said to be a *colloidal solution*. If the substance *dissolves*, as we say, in the liquid and assumes dimensions corresponding to those of individual molecules, having diameters of 1 $\mu\mu$ or less, we say that the substance is in a state of *molecular dispersion*, or *true solution*.

Colloidal solutions, as a rule, appear clear when viewed by transmitted light, i.e., looking straight through the solution in a test tube, but appear turbid when viewed by reflected light, i.e., with the test tube held above or below the level of the eye. The particles can be seen with the aid of the ultramicroscope and show a lively movement to and fro (Brownian movement).

The laws of their motion have been studied and found to correspond to that expected from the kinetic molecular theory. Colloidal chemistry, therefore, has served to bring the molecular hypothesis out of the realms of theory into the field of positive fact.

Many irreversible colloids separate out from their solutions as voluminous precipitates containing a large amount of water (*hydrogels*). Such hydrogels as, for example, those of ferric oxide, aluminium oxide, and silicon oxide, can also be obtained directly by chemical precipitation from solution. These precipitates contain a great deal more water than would correspond to their hydroxide formulas ($Fe(OH)_3$, $Al(OH)_3$, $Si(OH)_4$, etc.), and since the water thus contained does not show the characteristics of chemically combined water (compare the theoretical section on Hydrates preceding No. 144), these precipitates should be designated, according to van Bemmelen, as *oxide hydrogels*, or by their old name of *hydrated oxides*.

The change from the hydrosol to the hydrogel state is most simply brought about by the addition of an electrolyte. Many colloidal solutions are exceedingly sensitive to electrolytes (gold solution, No. 25); the most essential condition for the preparation of the solution must therefore be the absence of any unnecessary electrolyte. Even reversible colloids can be separated from their solutions by the addition of large amounts of an electrolyte; the process is termed "salting out," and is employed in the precipitation of proteins and dyestuffs (No. 24).

ADSORPTION COMPOUNDS.

Adsorption is the phenomenon shown by certain substances having a large surface (for example, wood-charcoal) of condensing gaseous or dissolved substances upon themselves. Adsorption is a special kind of natural phenomenon which is quite distinct from the process of solution.

It has been shown, especially by van Bemmelen, that the typical colloids exhibit a particularly high power of adsorption; and also that organized matter, such as plant fibers and decayed material like humus, possesses the same power. The latter classes of substances are, therefore, included among colloids, especially since in contrast to crystalloids they lack a definite form, bounded by rigid surfaces.

Among other instances in which adsorption may occur, the following are of especial importance. It may take place: (1) between liquids and solid substances (as when moisture is retained by many solid substances and particularly by hydrogels); (2) between dissolved substances and solids (as in the dragging down of dissolved salts by precipitates and in the adhering of fertilizer salts in the soil; cf. Nos. 22 and 23); (3) between dissolved reversible colloids and solid materials (as in numerous dyeing processes; No. 24). The combinations so produced are known as adsorption compounds.

For many adsorption processes, definite relations exist between the concentration in the solution of the substance adsorbed and the composition of the adsorption compound. Adsorption acts relatively more strongly the less concentrated the solution (cf. No. 22). Many adsorption compounds are of so specific a nature (for example, iodo-starch) that it has been only after the investigation of the quantitative relations between their composition and the conditions under which they are formed that their difference from true chemical compounds has been established. Such an exhibition of adsorptive power as this has also been designated as *affinity of condition.*

Different dissolved colloids can also mutually combine to form adsorption compounds: gold hydrosol, which is so exceedingly sensitive toward electrolytes, can, by the addition of a non-sensitive colloid such as gelatin, be itself made stable toward electrolytes; this would tend to show that a combination had taken place between the two kinds of dissolved colloids (cf. No. 25). Substances which act as gelatin does in this case are known as *protective colloids.*

Again, other colloids are capable of mutually precipitating one another out of solution.[1] Thus arsenic-sulphide-hydrosol and iron-oxide-hydrosol when mixed in the right proportions are both precipitated as a common adsorption compound (cf. No. 24, 4). This precipitating power arises from the same cause as another characteristic property which pseudo-dissolved substances have in common with suspensions: if suspensions or colloids are subjected to the action of a strong electric potential, a passage of the suspended material through the solution occurs, but this is of a very different nature from ionic migration. (*Convective transference.*) While, with electrolytes, the dissociated parts possess opposite electrical charges, here the opposite charges reside upon the pseudo-dissolved material and the solvent itself, respectively. It is a rule that two such colloids in order to precipitate each other must have charges of opposite sign when referred to that of the common solvent. (Example, zircon-gold-purple, No. 25.)

Finally, adsorption compounds can be produced by precipitating two colloids out of a common solution by the addition of an electrolyte. (Example, Purple of Cassius, No. 25.)

20. Colloidal Platinum, according to Bredig.

Connect two platinum wires of 1 mm. diameter, whose upper ends are insulated by glass tubes, with the terminals of the 110-volt lighting circuit, and insert an ammeter and a suitable resistance. Clamp one electrode so that its lower end dips into 100 to 150 c.c. of distilled water in a glass dish; hold the other electrode in the hand, and while it is immersed in the water, touch it to the first one and remove it to such a distance that a small arc can be maintained. The resistance should be regulated so that a current of 6 to 10 amperes will flow.[2] From the cathode the disintegrated platinum passes in grayish brown clouds into the liquid. It is not usually possible to preserve the arc for more than a short time, but it can be repeatedly started again by bringing the electrodes together, and then separating them; the process may be thus continued until the platinum solution is so dark as to be nearly opaque, or until it has become too hot. The platinum electrodes should never be held except by the insulated glass ends. If the experiment does not succeed well at first, add a trace of dilute alkali to the water. Finally, filter off the coarser platinum powder, and employ the solution in the following experiments:

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[1] W. Biltz, Ber. **37**, 1095 (1904).

[2] A technical ammeter with large capacity is used here. Before beginning the experiment, see that the wiring will safely bear the current required.

1. To a few cubic centimeters add a drop of a dilute salt solution. After a short time the colloidal metal separates out in the form of a powder (precipitation by an electrolyte).

2. Add some of the platinum solution to dilute hydrogen peroxide. A reaction takes place with evolution of oxygen, while a comparison sample of the hydrogen peroxide itself remains clear. Concentrated 30 per cent hydrogen peroxide, when treated with the platinum solution, decomposes at first slowly, then more rapidly, with rise of temperature, and finally with explosive violence. This is an instance of *catalysis;* i.e., the acceleration by means of a chemically indifferent substance (the platinum) of a reaction (the decomposition of hydrogen peroxide) which would of itself take place slowly.

3. To another portion of dilute hydrogen peroxide add a few drops of hydrogen sulphide water and then some platinum solution. This time no decomposition occurs; the catalyzer has temporarily lost its accelerating action in consequence of the presence of a third, likewise indifferent substance which acts as a poison. The catalytic property of the platinum depends upon the condition of the surface of the finely divided material; the action of the poison is due perhaps to an alteration in the condition of the surface.

21. Colloidal Antimony Sulphide.

Allow a cold 1 per cent solution of tartar emetic to drop from a dropping funnel into 200 c.c. of hydrogen sulphide water through which a fairly strong stream of hydrogen sulphide is kept passing. Antimony sulphide produced under these conditions does not form a precipitate, but remains in colloidal suspension as a deep-orange-colored pseudo-solution, that appears perfectly clear by transmitted light. First remove the excess of hydrogen sulphide by a stream of hydrogen, then place the solution in a dialyzing tube of parchment paper, and suspend the latter in a vessel of distilled water. If the tube is free from imperfections, almost none of the yellow material passes into the outer solution, while the salts present are gradually removed by diffusion. Replace the outside water with fresh water, at first every six hours, later every twelve hours, and continue the dialysis about four days.

Dilute a part of the antimony sulphide solution to ten times its original volume, and carry out the following experiments:

1. Place roughly equivalent, normal solutions of potassium chloride, barium chloride, and aluminium chloride in three burettes and add each, drop by drop, to three separate portions of 20 c.c. each of the colloidal antimony sulphide until the complete precipitation of the latter is accomplished. It may be necessary to repeat the experiment before the right end-point is obtained, noticing carefully when the precipitant causes the supernatant solution to change from yellow to colorless. It will be found that the largest amount of precipitant is required in the case of potassium chloride, the smallest in the case of aluminium chloride. The precipitating power of equivalent amounts of salts for colloids of this class increases with the valence of the cation.

2. Shake several portions of 10 c.c. each of the antimony sulphide for 1 minute with 2.0, 1.0, 0.5, 0.2, and 0.1 g. respectively of powdered barium sulphate. The pseudo-dissolved material is adsorbed by the solid. Determine what quantity of the barium sulphate is just sufficient for complete adsorption.

Test also, for comparison, the precipitating power of wood charcoal and animal charcoal.

22. Adsorption of Iodine by Charcoal. Adsorption Curve.

For a more accurate study of adsorption phenomena, charcoal is particularly well suited, since under ordinary conditions it is an indifferent substance, and has a constant surface. Place in each of four 200 c.c. glass-stoppered bottles 2 g. of washed, dried, and ignited animal charcoal and 50, 75, 90, and 95 c.c. of alcohol; then add 50, 25, 10, and 5 c.c. respectively of a normal alcoholic iodine solution, so that the volume in each bottle will be 100 c.c.

and the contents will differ only in the amount of iodine. After 24 hours, during which time the bottles should be frequently shaken, take 10 c.c. of the clear solution from each and determine the iodine content by titration with 0.1-normal sodium thiosulphate solution. The difference between the original weight present and the amount of iodine thus determined gives the quantity adsorbed by the charcoal. Arrange the results in a table and plot them on coördinate paper with the adsorbed amounts as ordinates and the corresponding amounts left in solution as abscissas. It is found that from dilute solutions relatively more iodine is adsorbed than from concentrated ones. This relation is quite general for adsorption equilibria, and can frequently be represented by the equation $\frac{c_1^n}{c_2} = k$, in which c_1 is the concentration of the adsorbed iodine, c_2 that of the unadsorbed iodine, and n and k are constants.[1] Since in these experiments the same volume and the same amount of charcoal are taken each time, the quantities of iodine determined may be used directly in place of c_1 and c_2 in the equation. Find by trial what value of n makes the quotient remain most nearly constant; n is greater than 1.

23. Lanthanum Blue.

The blue color which an iodine solution gives with starch depends on the formation of an adsorption compound between the two substances. This can be proved by a quantitative investigation of the adsorption curve. The same conclusion can be reached from the fact that another substance, the hydrogel of basic lanthanum acetate, which has no property in common with starch except the colloidal condition, gives precisely the same color reaction. The formation of lanthanum blue is made use of as a test for lanthanum. (Cf. No. 171.)

To a dilute solution of lanthanum acetate, or of lanthanum nitrate acidified with acetic acid, add a solution of iodine in potassium iodide, and then introduce ammonia cautiously, so as to not quite cause the yellowish-brown color of the iodine to disappear; warm very gently, and a dark-blue precipitate gradually forms.

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[1] This equation was proposed by von Bemmelen and later used by Küster and Biltz as well as by others. Freundlich has made it known more widely. Yet the equation itself is often over-emphasized; some reactions to which the equation appears to apply are not really adsorption reactions at all.

If a very dilute solution of lanthanum acetate is used, a blue colloidal solution is produced instead.

Prepare also a little iodo-starch from a very dilute starch solution and a few drops of iodine solution, and compare the colors.

24. Molybdenum Blue, Mo_3O_8.

Blue molybdenum oxide, Mo_3O_8, is soluble as a reversible colloid in water and behaves in this respect, as well as in its behavior towards vegetable and animal fibers, like many of the organic dyestuffs.

Dissolve 15 g. of commercial ammonium molybdate, $5(NH_4)_2MoO_4 \cdot 7\,MoO_3 \cdot 7\,H_2O$, in 250 c.c. of water, add 35 to 40 c.c. of 2-normal sulphuric acid, heat the solution to boiling, and keep boiling gently for 30 minutes to an hour, meanwhile introducing a stream of hydrogen sulphide. Reduction takes place, causing the appearance in a few moments of a dark-blue color. With a smaller amount of sulphuric acid a precipitation of molybdenum sulphide takes place; with more acid the yield becomes poorer. Filter from precipitated sulphur and subject the solution to dialysis for from 4 to 6 days (cf. No. 21), until the outside water is free from sulphuric acid, and is only faintly blue. Evaporate the contents of the dialyzing tube in a porcelain dish, at first over a free flame and finally on the water bath, until, after frequent stirring, the resinous, deep-blue residue has become a dry powder. Yield, 5 to 7 g.

The preparation is soluble without residue in water. Use the solution for the following experiments:

1. Boil a portion with a piece of undyed silk. The silk is colored blue. This dyeing experiment can also be carried out with the undialyzed solution.

2. Repeat Experiment 1 with the addition of a considerable amount of sodium sulphate. More of the coloring matter is taken up by the silk. This is due to the salting-out action of the electrolyte.

3. Shake a little of the solution with some freshly-precipitated, washed aluminium hydroxide. A mixture of molybdenum blue and hydrated aluminium oxide is precipitated (a lake) and the solution becomes lighter colored. Hydrogels can thus be dyed like fabrics.

4. Mix a few cubic centimeters of dilute molybdenum blue solu-

tion, drop by drop, with a colloidal solution of zirconium oxide.[1] After enough of the former has been added, a molybdenum-blue-zircon lake is precipitated. Regarding the mutual precipitation of colloids, see p. 42.

25. Colloidal Gold Solutions; Precipitating Colloids and Protective Colloids.

During recent years, gold solutions have been used with great success, particularly by Zsigmondy, in making clear the nature of the various properties of colloidal suspensions. Red colloidal solutions of gold can be prepared by electrical disintegration of the metal or by reduction of gold salts in various ways. The red color of gold-ruby glass is likewise due to colloidal gold. The adsorption compound of colloidal gold and tin oxide hydrogel, called *Purple of Cassius,* serves for the qualitative detection of gold. (Cf. No. 9.)

1. *Colloidal Gold according to Zsigmondy.*[2] Mix together in a round-bottomed, 300–400 c.c. flask of Jena glass, 120 c.c. of pure, distilled water[3] and 2.5 c.c. of chlorauric acid solution (prepared by dissolving 0.6 g. of $HAuCl_4 \cdot 3\ H_2O$ crystals in 100 c.c. of distilled water) and add 3.0 to 3.5 c.c. of 0.18 normal, pure potassium carbonate solution. After this, add about 0.5 c.c. of an ethereal phosphorus solution, prepared by saturating ether with phosphorus and finally diluting to five times the original volume with ether. If the mixture is allowed to stand several hours, it will gradually turn brown, often showing a blue or black color as well, and finally turn red. After about 24 hours at room temperature, a fairly homogeneous colloidal solution of gold will be obtained with the particles of gold so small that they cannot be seen with the ultra-microscope (amicrons). The reduction of the gold from the tervalent state, in which it exists in chlorauric acid, takes place more rapidly if the liquid is heated to boiling after the introduction of the ethereal solution of phosphorus. Then, after the red colora-

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[1] Pseudo-solutions of zirconium oxide can be prepared by dialyzing a solution (about 16 per cent) of zircon nitrate for about 5 days with frequent change of water.

[2] R. Zsigmondy, Z. Anal. Chem. **40**, 697 (1901). The most beautiful gold solutions can be obtained by this classic but very difficult procedure.

[3] This preparation is a difficult one. It is best to use distilled water which has been redistilled, after adding some potassium permanganate, using a *silver* condenser and a receiver of Jena glass.

tion has been obtained, the ether can be driven off completely and air introduced to oxidize the excess phosphorus, without injury to the gold colloid (hydrosol). This preparation of colloidal gold solution is very sensitive to external conditions; it is not possible to produce equally good solutions in all laboratories.

2. *Colloidal Gold by Reduction with Carbon Monoxide.* Prepare carbon monoxide by heating oxalic acid crystals with concentrated sulfuric acid, and passing the gas through sodium hydroxide solution to remove carbon dioxide. Pass a slow stream of the carbon monoxide into 120 cc. of 0.03% chlorauric acid. There is produced a violet color which changes to violet-red and later to a dark red. Do not carry the reduction too far, as the solution will then assume a permanent violet color.

3. *Colloidal Gold by Reduction with the Hydrogen Flame.*[1] It is easy to prepare a colloidal gold solution by merely directing a pointed hydrogen flame, 1 to 2 cm. long, against a 0.03% solution of chlorauric acid contained in a wide, porcelain dish. After about five minutes the solution begins to be colored; soon a rich red color is produced. Occasional stirring hastens the formation of the colloidal gold.

Use a gold solution prepared by any one of these methods in the following experiments.

I. *Synthesis of Purple of Cassius.* From a mixture of colloidal stannic oxide and colloidal gold, the gold-stannic oxide adsorption compound is precipitated on the addition of electrolytes. In order to prepare the colloidal stannic acid solution, allow 5 c.c. of tin tetrachloride (No. 50) to become hydrolyzed by the addition of 150 to 200 c.c. of water, and pour this solution into 500 c.c. of water to which a few drops of ammonia have been added. Dialyze the clear mixture for five days (cf. No. 21), changing the outside water two or three times daily, until it shows no test for chlorides. If during this process a hydrogel separates in the dialyzing tube, it may be peptonized (see p. 40) in a beaker by the addition of about three drops of ammonia, whereupon, after a time, the jelly will go over into a perfectly clear hydrosol. A mixture of this hydrosol with an equal volume of gold solution remains unchanged, but on addition of a salt (ammonium chloride) a beautiful deep-reddish-purple precipitate is formed which can be filtered off; the compound is characterized by its solubility in ammonia.

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[1] J. Donau, Monatsh. **34**, 949 (1913). Colloidal solutions of silver, platinum and molybdenum blue can be prepared by this method.

II. *Zircon-gold-purple.* Treat 130 c.c. of a boiling colloidal gold solution with 28 c.c. of a boiling colloidal zircon solution (see footnote to No. 24). A precipitation of zircon-gold-purple takes place even without the addition of an electrolyte. In the cold the precipitate forms slowly. If the deposition is incomplete, preliminary tests must be made with small portions to find the right proportions in which to mix the above solution.

III. *Gold Solution and Protective Colloids.* Treat 10 c.c. of colloidal gold solution with a few drops of dilute hydrochloric acid; a blue coloration is first produced, later sedimentation of the metal.

Repeat the experiment after first adding one drop of a dilute gelatin solution (0.2 per cent) to the colloidal gold; no change whatever in the color or the stability of the gold solution is observed.

26. Hydrogels as Semipermeable Membranes.

The separation of colloids and electrolytes by dialysis depends on the colloidal nature of the parchment wall, which is impervious to other colloids. Certain colloids are impervious even to truly dissolved substances but still pervious to water. By means of membranes of such semipermeable material a solute can be separated from its solvent, and thus the osmotic pressure of the dissolved substance can be both demonstrated and measured. Cupric ferrocyanide has been found especially suitable as a semipermeable colloid. (Pfeffer, 1877.)

1. *Cupric Ferrocyanide Membrane.* Let a drop of a cold, saturated potassium ferrocyanide solution run from a fine, glass capillary into a 0.5-molal copper sulphate solution, and detach it by means of a slight motion, so that it sinks to the bottom of the vessel. The drop has at the moment of its entrance into the solution become surrounded with a thin film of cupric ferrocyanide, which keeps growing at the cost of the dissolved components. Since, however, the concentration of the solute within the membrane is greater than that of the copper sulphate outside, the membrane expands in consequence of the pressure caused by the water entering through the walls. The membrane is at first transparent and traversed by brown veins. A uniform growth can be brought about by occasional, gentle stirring of the copper sulphate solution. As the cell keeps expanding a point is reached when the specific gravity of its contents having grown less through

entrance of water, the cell rises to the surface of the solution, and remains there until, after ten or fifteen minutes, the constant thickening of its walls so increases its weight as to make it once more sink, and this time permanently.

2. *Membranes of Colloidal Silicates of the Heavy Metals.* Dilute some commercial water-glass solution until a specific gravity of 1.1 is obtained. Into about 100 c.c. of this solution in a narrow beaker, drop small particles of various salts, such as copper sulphate, aluminium sulphate, ferric chloride, nickel nitrate, cobalt nitrate, manganous sulphate, lead nitrate, and uranyl nitrate. Within a few minutes the particles begin to swell and to send out shoots which branch and grow toward the surface of the liquid until the whole beaker is filled with what appear to be bright colored algæ growths. The salt, on being thrown into the solution, begins at once to dissolve, and at the surface of contact between this solution and the silicate solution, an insoluble semi-permeable film of metal silicate is formed. The dissolved salt within exerts an osmotic pressure against this film, and forces it to expand, while the water which is thereby drawn in through the film dissolves more of the salt. The osmotic pressure is thus maintained and the film is continuously forced to expand until it bursts in places and forms outgrowths and side-arms.

CHAPTER III.

SIMPLE COMPOUNDS.

UNDER the designation *simple compounds* are included all compounds containing but two elements, with the exception, however, of the persulphides, peroxides, polyhalides, etc., which are considered to have complex cations (Chap. IV). The metal hydroxides and cyanides, in which the radicals OH and CN behave as single elements, are also classed as simple compounds.

METHODS OF PREPARATION. Simple compounds are prepared:

(1) Synthetically from the elements:

$$Br_2 + H_2 = 2\,HBr \text{ (No. 35a).}$$

Cf. also Cerium Hydride (No. 32); FeI_2 (No. 39); $FeCl_3$ (No. 42); $CrCl_3$ (No. 44); S_2Cl_2 (No. 45); PCl_3 (No. 46); BiI_3 (No. 48); $BiBr_3$ (No. 49); $SnCl_4$ (No. 50); $SiCl_4$ (No. 51); P_2S_5 (No. 54); HgS (No. 55); Mg_3N_2 (No. 61); Mg_3P_2 (No. 63).

Frequently the synthetic preparation of compounds between two elements takes place in stages:

$$P + 3\,Cl = PCl_3,$$
$$PCl_3 + 2\,Cl = PCl_5. \quad \text{(No. 46)}$$

Cf. also SO_3 (No. 28); $SbCl_5$ (No. 47); SnS_2 (No. 56).

(2) By the interaction of two substances, each containing one of the elements which are to be combined:

(*a*) By the action of an element upon a compound:

$$Fe + 2\,HCl = FeCl_2 + H_2. \quad \text{(No. 43)}$$

Cf. also $AlCl_3$ (No. 43).

(*b*) By the chemical reaction between two compounds (double decomposition or metathesis), as, for example, in the precipitation of a sulphide from the solution of a metallic salt by means of hydrogen sulphide:

$$CuCl_2 + H_2S = CuS + 2\,HCl.$$

Cf. MnS (No. 57); TiS_2 (No. 58); CrN (No. 62); and BrH (No. 35b).

(3) By the breaking down of more complicated compounds:

$$2\,HNO_3 = H_2O + N_2O_4 + O \text{ (No. 29)}$$

Cf. also Cr_2O_3 (No. 30); Cu_2O (No. 31); copper hydride (No. 33); cyanogen (No. 59); BaS (No. 87).

Certain simple compounds which were formerly prepared by double decomposition, or by the breaking down of more complicated compounds, are now most advantageously obtained directly from the elements, even industrially; both because the requisite conditions for their formation are now better understood and because some elements are far more accessible than formerly.

Thus sulphuric acid anhydride is now prepared directly by the contact process (No. 28), nitric oxide from the elements in the atmosphere (combustion of air), ammonia from nitrogen and hydrogen, and aluminium chloride from the metal (cf. No. 43.)

Reactivity and Degree of Dissociation. It is a general principle that the reactivity of a substance is determined by a previous breaking down (dissociation), to a greater or less extent, in the same sense as that in which the reaction in question takes place. Phosphorus pentachloride, for example, has a chlorinating effect, and sulphur trioxide an oxidizing effect, only when under the prevailing conditions the one is partly dissociated into free chlorine, the other into free oxygen, even in the absence of any substance to be chlorinated or oxidized. Conversely, a tendency shown by substances to enter into reaction may be considered as an indication of the preëxistence of a corresponding dissociation. The dissociation of binary substances, which in fact often takes place in stages, is essentially the reverse of their synthesis.

$$PCl_5 = PCl_3 + Cl_2$$
$$PCl_3 = P + 3\,Cl$$
$$2\,SO_3 = 2\,SO_2 + O_2 \quad \text{(No. 28)}$$

Dissociation and State of Equilibrium. If it is true that reactivity is dependent upon a certain ability to dissociate, it becomes important to study the conditions favoring the formation and those favoring the decomposition of substances. To take a concrete example, — When does the reaction

$$2\,SO_2 + O_2 = 2\,SO_3$$

take place, and when

$$2\,SO_3 = 2\,SO_2 + O_2?$$

In this connection, another principle which is likewise of very general importance has been established, — namely, that a reaction never takes place completely in one direction; at most the chemical change may proceed *chiefly* in a definite direction until when the reaction comes to a standstill (i.e., when equilibrium is reached) the products of dissociation and the undissociated compound exist together side by side, forming the so-called *equilibrium-mixture.* The percentage composition of an equilibrium-mixture is characterized by the fact that the same values are obtained irrespective of whether at the start a mixture of the pure components or the pure compound itself is present. Thus, for example, the same mixture of SO_3, SO_2, and O_2 is obtained whether equivalent amounts (e.g., formula weights) of SO_2 and O_2 are allowed to react, or an equivalent quantity of SO_3 is allowed to decompose under the same conditions of temperature and volume.

$$2\,SO_3 \rightleftarrows 2\,SO_2 + O_2$$

should be read: sulphur trioxide "in equilibrium with" sulphur dioxide and oxygen.

Inasmuch as all reactions are, strictly speaking, reversible, it is theoretically impossible to prepare perfectly pure compounds; for a compound can only exist as a stable substance when it is in equilibrium with its products of dissociation. For practical purposes, however, it is true that (1) in the equilibrium mixture the percentage content of dissociation products, or in the other case the fraction of undissociated substance, is frequently so extremely small that it becomes negligible, and that (2) the rate at which certain substances decompose after they have once been prepared "pure" is often so extremely slow that measurable quantities of the dissociation products are formed only after a very long time.[1]

MASS-ACTION LAW. The state of equilibrium which combining or decomposing substances reach is dependent (1) upon the nature of the reacting substances, (2) upon their masses, and (3) upon the temperature. The influence exerted by the masses upon the state of equilibrium can be expressed mathematically by the so-called Law of Mass Action (Guldberg and Waage, 1867). According to this law, the product of the concentrations of the substances which are upon the right-hand side of the sign of equilibrium, divided by the product of the concentrations of the substances on the left-hand side, is a constant at a given temperature. The concentration is usually expressed as the number of gram-molecules of substance which are contained in a unit of volume. If A is the formula of a substance, it is customary to express the concentration of A by inclosing it in brackets [A]; then if (A) represents the actual amount of substance present expressed in gram-molecules, and v the volume, we have

$$[A] = \frac{(A)}{v}$$

If A and B are two substances which by reacting together form two new substances C and D, with which they finally come to equilibrium,

$$A + B \rightleftarrows C + D,$$

then the mass-action law is expressed as follows:

$$\frac{[C]\,[D]}{[A]\,[B]} = K.$$

If, however, two or more molecules (a, b, etc., being the numbers) of any of the substances enter into the reaction, then the concentration of these substances must be taken a, b, etc., times in the mass-action-law equation. Thus if a molecules of A react with b molecules of B to form c molecules of C and d molecules of D, the equation becomes:

$$\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K.$$

APPLICATION OF THE MASS-ACTION LAW. The value of the mass-action law for the manufacturing chemist becomes apparent when with its aid the yields are predicted that can be obtained in the preparation of a substance at a given temperature but with varying proportions of the reacting materials. This is particularly well illustrated by measurements of Bodenstein and Pohl with regard to the contact-process for the manufacture of sulphuric acid. Sulphur dioxide and oxygen react within a reasonable interval of time to form sulphur trioxide only when in the presence of catalyzers; the presence of the catalyzer, however, has no effect upon the equilibrium which is finally reached.

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3.$$

---

[1] In old collections of organic preparations, the amount of impurities which have arisen from a self-decomposition of the material is often very considerable.

If, as before, v represents the volume of the gas-mixture, and the formulas inclosed in parentheses the number of gram-molecules of substance present when equilibrium is reached, then for a given temperature the mass-action law gives the relation:

$$\frac{\frac{(SO_3)^2}{v^2}}{\frac{(SO_2)^2}{v^2}\frac{(O_2)}{v}} = K,$$

and the "efficiency" of the reaction, i.e., the ratio of the trioxide formed to the unchanged dioxide, is:

$$\frac{(SO_3)}{(SO_2)} = \sqrt{\frac{K\,(O_2)}{v}}\,.$$

It is evident from this last expression, that it is favorable to the yield if as pure oxygen as possible (small v, little diluent of indifferent gas) and as much oxygen as possible (high concentration of O_2) is present. That this conclusion is correct is shown by the following table, in which the yield (i.e., the actual quantity of SO_3 obtained, compared with what would result if the entire amount of the SO_2 could be oxidized) is given in per cent by volume. In the first case a mixture composed of the theoretically correct proportions of sulphur dioxide and oxygen was taken, in the second the same mixture diluted with nitrogen, and in the third case sulphur dioxide together with an excess of oxygen. The measurements were made at 500°.

	Per cent N_2.	Per cent SO_2.	Per cent O_2.	Yield in per cent SO_2 oxidized.
1	0.	66.67	33.33	91.3
2	89.50	7.00	3.5	81.2
3	0.	7.00	93.00	98.1

For the formation of ammonia from the elements:

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

the mass-action law gives:

$$\frac{\frac{(NH_3)^2}{v^2}}{\frac{(N_2)}{v}\cdot\frac{(H_2)^3}{v^3}} = K.$$

The equilibrium quantity of ammonia is:

$$(NH_3) = \frac{1}{v}\sqrt{K(N_2)\,(H_2)^3}.$$

The yield of ammonia, therefore, increases with decreasing volume,

v, or, in other words, as Nernst predicted from the theory and Haber has found in practice, the yield increases as the pressure increases. This is shown very clearly by the values given for the yields of ammonia obtained by Haber in experiments with the equilibrium mixture of 3 vol. H_2 to 1 vol. N_2.

t.	1 Atm.	30 Atm.	100 Atm.	200 Atm.
400°	0.44%	10.7%	25.1%	36.3%
600	0.049	1.43	4.47	8.25

Further applications of the mass-action law are illustrated in the preparation of nitrogen peroxide (No. 29), hydrobromic and hydriodic acids from the elements (No. 35), and phosphorus pentachloride and trichloride (No. 46); cf. also, Dissociation of Electrolytes, p. 66.

DEPENDENCE OF EQUILIBRIUM CONSTANTS UPON THE TEMPERATURE. It is also apparent from the above expression that the yield in the contact process is dependent on the value of the constant, K; if K can be made greater, the proportion of SO_3 is increased. The value of K depends upon the temperature, and its variation can be predicted with the aid of thermochemical data and the principles of thermodynamics.

Chemical reactions are, from a thermochemical standpoint, divided into two classes: those in which heat is evolved, or set free (exothermic reactions), and those in which heat is absorbed, or used up (endothermic reactions). Endothermic compounds, or, in other words, those in the formation of which from their elements heat is absorbed, are far less common (cf. cyanogen, No. 59, and hydrogen peroxide, No. 67). Experience has shown that the conditions for the formation of endothermic compounds are more favorable at high temperatures, while for exothermic compounds the reverse is true. Since in the formation of a substance the size of the constant, K, is, under otherwise equal conditions, a measure of the yield, it seems plausible that in the case of exothermic reactions the value of K diminishes with rise of temperature, whereas in endothermic reactions it increases.

According to van't Hoff, there exists between the heat of reaction Q, the absolute temperatures T_1 and T_2, at which the reaction takes place, and the corresponding equilibrium-constants K_1 and K_2, together with the gas constant R, the exact relation:

$$\ln K_2 - \ln K_1 = \frac{Q}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

from which it follows that when $T_2 > T_1$, and the value of Q is positive (exothermic reactions), K_2 becomes smaller than K_1, and for negative values of Q (endothermic reactions) K_2 is greater than K_1. This is based upon the assumption that Q is independent of the temperature at which the reaction takes place. Whether this is true or not must be ascertained in the case of each reaction studied. In the synthesis of sulphuric anhydride this has been found to be practically true; and it is therefore possible, when the analysis of the equilibrium mixture at a given temperature is known, to compute the composition of the equilibrium mixture at any other temperature. The equilibrium-constants, as above defined, for the sulphuric acid contact-process have been found to be as follows:

t.	*K.*	*t.*	*K.*
528°	$645. \times 10^2$	727	2.82×10^2
579	$131. \times 10^2$	789	0.794×10^2
627	31.6×10^2	832	0.357×10^2
680	8.93×10^2	897	0.123×10^2

In accordance with the positive heat of reaction, $Q = 21{,}700$ calories, a rapid diminution in the value of *K* is observed.

The practical application of the theory in the manufacture of sulphuric acid is shown by the following yields calculated for various mixtures at different temperatures:

Composition of Reacting Mixtures.		Yield of SO_3 at			
SO_2	O_2	400°	500°	700°	900°
66.67	33.33	98.1	91.3	51.5	16.0
14.00	86.00	99.8	97.9	69.8	24.4
2.00	98.00	99.8	98.2	71.2	25.6

It is, therefore, more important that the process should be carried out at a relatively low temperature than that an excess of oxygen should be employed. On the other hand, the temperature cannot be made too low, as then the rate at which the reaction takes place, even in the presence of a catalyzer, becomes too small.

The so-called "blast-furnace equilibrium," $2\,CO + O_2 \rightleftarrows 2\,CO_2$, is displaced with increase of temperature, and the reaction proceeds more in the direction from right to left, because here again the heat of reaction is positive; cf. No. 1.

OXIDES.

27. Liquid Sulphur Dioxide.

Sulphur dioxide is prepared technically by burning either sulphur or pyrite. On a small scale, it is obtained by the reduction of concentrated sulphuric acid, or its anhydride, which when hot has a strong oxidizing power:

$$SO_3 + Cu = SO_2 + CuO.$$

The reduction with copper takes place also to a slight extent, according to the equation:

$$SO_3 + 4\,Cu = CuS + 3\,CuO.$$

The copper oxide, as fast as it is formed, dissolves in the sulphuric acid, forming copper sulphate. It is essential for the decomposition that the sulphuric acid should be hot and that it should be concentrated, whereby its content of SO_3 is increased; the nature of the reducing agent is less important, for the copper may be replaced by other metals or even by carbon.

Sulphur dioxide can be condensed to a liquid (boiling-point $-10°$) by cooling the gas in a mixture of ice and common salt.

Heat 50 g. of copper turnings in a round-bottomed flask with 200 g. of concentrated, commercial sulphuric acid until the boiling-point of the latter is nearly reached. Lower the flame as soon as gas is given off freely. Pass the gas through a wash bottle containing concentrated sulphuric acid, and into a second empty wash bottle which is surrounded with a mixture of three parts of ice to one of salt, and in which the sulphur dioxide condenses to a liquid.

When the evolution of the sulphur dioxide slackens, pour the liquid from the evolution flask into an evaporating dish before it has a chance to solidify, and allow it to cool by standing over night. In the morning decant the liquor from the mass of crystals which have separated, dissolve the crystals in as little boiling water as possible, and filter off any insoluble black powder on a large plaited filter. Copper vitriol, $CuSO_4 \cdot 5\ H_2O$, separates from the filtrate in well-defined crystals; collect them in a filter funnel and evaporate the mother liquor to obtain a second, and finally a third, crop of crystals. When the product has been dried as much as possible by suction, place it in an evaporating dish, which is covered with filter paper, and allow it to dry for several days at the room temperature.

The sulphur dioxide, as prepared above, always contains some sulphuric acid, fumes of which are carried over mechanically by the gas from the evolution flask, and are not entirely kept back by the first wash-bottle; immediately after being prepared, therefore, the sulphur dioxide should be purified by distillation. Close one tube of the wash bottle which contains it, and connect the other tube by means of a short piece of rubber with a glass tube which is bent at right angles, and whose vertical arm is drawn out to an internal diameter of about 0.2 cm. (Fig. 12). Introduce this narrow tube nearly to the bottom of a thick-walled sealing tube, 0.4 to 0.5 cm. wide, which is sealed at the bottom, and drawn out a little at a point about 18 cm. above the lower end. This tube is prepared, cleaned, and dried before beginning the distillation; care must be taken to round the lower end and to make the constriction without lessening the thickness of the walls at any point.

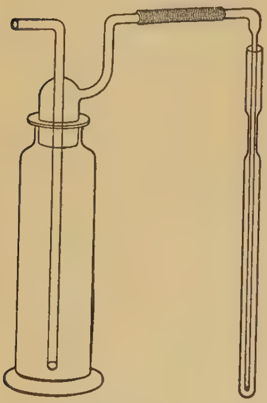

Fig. 12.

In order to distil the sulphur dioxide, transfer the wash bottle from the freezing mixture to a bath of water at room temperature, and place the thick-walled tube, which now serves as the receiver, in the freezing mixture. The sulphur dioxide soon begins to distil. When the receiver is about half filled, stop the distillation and seal the tube at the constriction, taking great care that the strength of the walls is not lessened thereby. While the tube is being sealed it must be kept in the freezing mixture; the tube and bath together may be held by a second person at a proper distance from the blast lamp. The tube must be allowed to cool while resting in a perpendicular position so that the liquid sulphur dioxide does not come in contact with the hot parts of the glass.

28. Sulphur Trioxide by the Contact Process.

The fact that sulphur dioxide will combine with oxygen when in the presence of finely divided platinum was known in the first half of the last century. Cl. Winkler showed as early as 1875 that, by means of such a contact-process, sulphuric acid could be made on an industrial scale from mixtures of sulphur dioxide and oxygen. It was not until nearly the close of the century, however, that the doubts with regard to the feasibility of manufacturing sulphuric anhydride on a large scale from the gases evolved in the roasting of pyrite were overcome; then the Badische Aniline- und Sodafabrik made public the most favorable temperature for this process and directed the attention of a wide circle of chemists to the problem of freeing the gases from catalyzer poisons (cf. No. 20), particularly arsenic compounds.

Sulphur trioxide exists in two allotropic modifications: as a mobile liquid (boiling-point 46°) which forms crystals on being sufficiently cooled (freezing-point 15°), and as a white asbestos-like mass which on warming volatilizes without previously melting. The latter is the more stable modification; liquid sulphur trioxide on standing goes over slowly of itself, or more rapidly in the presence of a trace of sulphuric acid which acts as catalyzer, into this asbestos-like condition.

The asbestos-like form when dissolved in phosphorus oxychloride is bi-molecular, whereas the liquid sulphur trioxide proves to be monomolecular when studied in the same way. It seems probable, therefore, that the solid form is a polymer of the liquid.

Make a slight bend in a 40 cm. long combustion tube at a point about 6 cm. from one end, and insert the bent end in one opening of a two-necked globular receiver (Fig. 16); to the other neck connect a glass tube leading to the ventilating flue of the hood under which the apparatus is constructed. Make the joints tight by means of asbestos cord. Close the front end of the combustion tube with a cork through which one arm of a T-tube is inserted in order that sulphur dioxide and oxygen may be introduced at the same time. Fill a section of the combustion tube, 12 to 15 cm. long, with loosely-packed, platinized asbestos which is prepared by moistening the required amount of asbestos with 5 c.c. of 10% chloroplatinic acid solution, drying and igniting the mass. After the experiment the platinized asbestos can be purified by washing and again igniting, and it is then ready for use again. The whole apparatus must be perfectly dry; even the asbestos cord with which the joints are made tight must be previously ignited.

Place the combustion tube in an asbestos chamber (cf. Fig. 4), whose edges measure 15, 4.5, and 4.5 cm. respectively. There should be a wide slit in the bottom for the entrance of the flame, and an opening in the cover to carry away the combustion products. Place a wide burner at some distance below the combustion tube, and regulate the flame to maintain the temperature of the platinized asbestos at about 400°. This temperature may be read with a mercury thermometer which has been filled under pressure, or it may be estimated quite closely with a 360° thermometer if the latter, upon being placed inside the asbestos chamber, shows but a slow rise of its thread above the 350° mark.

Pass oxygen from a steel cylinder or a gasometer through a wash bottle containing concentrated sulphuric acid, which serves to dry the gas and at the same time to show the speed with which it is being drawn. Admit the oxygen through one arm of the T-tube into the combustion tube, and through the other branch of the T-tube introduce sulphur dioxide which is generated by the action of 400 g. concentrated sulphuric acid upon 100 g. copper. This gas must likewise be passed through sulphuric acid, and in addition through a tube loosely filled with glass wool in order to free it from the spray mechanically carried along from the generating flask. Regulate the flow of the two gases so that a little more oxygen than sulphur dioxide passes into the contact tube. Keep the receiver immersed in ice water; sulphur trioxide collects abundantly either in the liquid modification or in the asbestos-like form. The experiment takes about three hours.

For the following experiments use the liquid form. In case the asbestos-like form has been obtained, loosen it with a glass stirring rod and place a layer of it about 1 cm. deep in each of three test-tubes; add (*under the hood*) a drop of concentrated sulphuric acid to each tube, heat just to the melting-point, and then allow to cool. To one test-tube add flowers of sulphur from the point of a knife blade; to the second, powdered selenium; and to the third, iodine. In the first test-tube an indigo-blue solution is formed, in the second a bluish green, and in the third likewise a bluish green, or, if considerable iodine has been added, a brown solution. The compounds, S_2O_3 and $SSeO_3$, are produced in the first and second tubes respectively.

Oxidation of Naphthalin with Sulphuric Acid.

The dissociation of sulphur trioxide, $SO_3 = SO_2 + O$, in opposition to the reaction of its synthesis by the contact process, is frequently utilized for technical and analytical purposes; by an increase of temperature, and by the presence of catalyzers, such as mercury or copper salts, the oxidizing action is considerably accelerated. Instead of sulphur trioxide, fuming sulphuric acid or even ordinary concentrated sulphuric acid may be employed, although the effect is not then so readily obtained.

The most important technical utilization of this oxidizing power of fuming sulphuric acid is in the transformation of naphthalin into phthalic acid, the latter being used in the preparation of artificial indigo:

$$\underset{\text{Naphthalin}}{C_{10}H_8} + 9\,O = \underset{\text{Phthalic Acid}}{C_8H_6O_4} + H_2O + 2\,CO_2.$$

Place 5 g. naphthalin, 1 g. mercury, and 80 g. concentrated sulphuric acid in which the remainder of the above sulphur trioxide has been dissolved (or 80 g. of commercial, fuming sulphuric acid) in a 300 c.c. retort, and heat the mixture slowly, almost to boiling, on a Babo funnel. Insert the neck of the retort into a small flask, which serves as a receiver, and cool the latter with water. A white sublimate of phthalic anhydride soon appears in the upper part and neck of the retort, and the odor of sulphur dioxide becomes apparent. From time to time drive the sublimate over into the receiver by fanning the top and neck of the retort with the flame of a Bunsen burner. When, at the end of two or three hours, nothing further passes over, decant off the sulphuric acid which has distilled into the receiver and recrystallize the phthalic anhydride, from 75 to 100 c.c. of water. The filtrate from the first crop yields more crystals on evaporation.

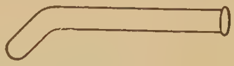

Fig. 13.

Dry the phthalic acid thus obtained, and distil it in a test-tube held nearly horizontally, the closed end of which is bent downward at a slight angle, as shown in Fig. 13. Water is split off from the molecule during the sublimation, and beautiful needles of phthalic anhydride (melting-point 128° C.) are formed. By another crystallization from water, 2 to 3 g. of pure, perfectly white phthalic acid are obtained.

For the characterization and identification of the phthalic acid, mix a little of it with equal amounts of resorcinol and anhydrous zinc chloride. Heat this mixture slowly in a small, dry test-tube over a small flame until it sinters and then melts. After heating a minute longer, cool the brownish-red fusion and dissolve it in a little alcohol. Pour the solution thus obtained into a large beaker containing distilled water, and add a few drops of caustic soda solution. A deep-yellow solution is obtained which, by reflected light, shows a beautiful green fluorescence (synthesis of fluorescein).

29. Nitrogen Dioxide.

Place 40 g. of coarse lumps of arsenic trioxide in a flask, add 50 g. of concentrated nitric acid (sp. gr. 1.4), and heat the mixture moderately upon a sand bath (or Babo boiling funnel). Lead the gases evolved successively through an empty wash-bottle, a U-tube containing glass wool, a second empty wash-bottle, and finally into a third wash-bottle (surrounded with ice) in which the oxides of nitrogen are condensed. A mixture of nitrogen dioxide, nitrogen trioxide,[1] and nitric oxide is obtained.

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[1] Nitrogen trioxide N_2O_3 can exist only in the liquid condition. It is unstable, and when vaporized dissociates into NO and NO_2 (or N_2O_4). v. Wittorff, Z. anorg. Chem. **41**, 85 (1904).

After the evolution of gas from the flask has ceased, pass a current of oxygen through the condensed liquid in the wash-bottle, still keeping it surrounded with ice, until the color becomes a pure yellowish brown; only a small amount of the nitrous gases are lost during this operation. If it is desired to preserve the preparation, heat the flask containing the liquid nitrogen dioxide cautiously by means of lukewarm water and distil the liquid into a sealing tube, in exactly the same manner as with sulphur dioxide (p. 57). Boiling-point 22° C.

Cork stoppers and rubber tubing are energetically attacked by the oxides of nitrogen. Therefore, in fitting up the above apparatus, select corks which fit tightly and protect them with a coating of vaseline; where the use of rubber connections is unavoidable, bring the ends of the glass tubing close together.

Gaseous nitrogen dioxide is always mixed with considerable nitrogen tetroxide, N_2O_4, formed by *association* of the dioxide molecules. The mixture is light brown at room temperature; on being heated it becomes darker as a result of progressive *dissociation:* $N_2O_4 \rightarrow 2\ NO_2$, but on being heated more strongly (above 130°) it becomes lighter in color owing to the decomposition of the dioxide into nitric oxide, NO, and oxygen. These changes in color can be shown by a simple experiment. Take a 25–30 cm. long glass tube of difficultly-fusible glass, with about 1 cm. outside diameter, and introduce a small amount of liquid nitrogen dioxide by the method described for sulphur dioxide in Preparation No. 27. After all the liquid has been allowed to evaporate, seal the tube filled with the vapor. For the nitrogen dioxide to be completely dry at this point, phosphorous pentoxide should have been added to the liquid in the wash bottle before distilling it into the experimental tube. Clamp the tube in a horizontal position and heat it in the middle with a broad flame from a Bunsen burner until the gas in this part of the tube appears colorless ($NO + O_2$); the gas will be dark brown on both sides of the colorless zone (NO_2), while the outer portions of the gas will appear light brown ($NO_2 + N_2O_4$).

Arsenic acid may be obtained from the residue in the evolution flask. Complete the oxidation by further heating with concentrated nitric acid, and evaporate the solution to a fairly thick sirup. If exactly the right concentration of the sirupy solution is obtained, it will form a nearly solid mass of crystals of arsenic acid on standing in the ice chest.

30. Chromic Oxide in the Dry Way from a Chromate.

The preparation of chromic oxide by the reduction of an aqueous solution of a chromate to one of a chromic salt, with subsequent precipitation and ignition of chromic hydroxide, is not a convenient process because of the difficulty and tediousness of filtering and washing the very voluminous precipitate. The method originated by Wöhler, 1827, which is that given in the following directions, is, therefore, preferable. The chromate is heated in a crucible with ammonium chloride, whereby the ammonium radical is oxidized to water and nitrogen while the chlorine combines with the alkali metal of the chromate.

Mix 147 g. potassium dichromate (one-half mol.) intimately with an equal weight of ammonium chloride, and heat the mixture in a clay crucible, in a charcoal furnace, until no more vapors are given off. After cooling, boil the brittle contents of the crucible repeatedly with fresh portions of water until all the soluble salt has been removed. Compute the yield of the dried preparation in percentage of the theoretical. Dependent preparation, Chromium No. 3.

31. Cuprous Oxide.

In a 1750 cc. Erlenmeyer flask mix a solution of 55 grams of copper sulphate crystals in 500 c.c. of water with one of 25 grams of hydroxylamine hydrochloride in 125 c.c. of water. While cooling in running water and shaking vigorously, slowly add a solution of 55 grams of stick potassium hydroxide in 750 c.c. of water. A yellow precipitate of cuprous oxide will form. After the precipitate has settled well, pour off the supernatant liquid and wash the precipitate by decantation four times with very dilute hydrochloric acid and then with pure water until the washings show no test for either chloride or sulphate. For the decantations, it is well to support the flask in an inclined position so that the precipitate is not disturbed when the liquid is poured off. Finally drain the precipitate with suction, wash with a little alcohol and finally with some ether. Dry in a vacuum desiccator, which causes a slight darkening. Yield about 14 grams.

HYDRIDES.

A few metals combine directly with hydrogen at definite temperatures to form hydrides (e.g., cerium hydride No. 32).

Copper hydride is formed in aqueous solution by treating cupric salts with very strong reducing agents (No. 33).

Certain products which are formed by the occlusion of hydrogen on the part of some of the heavy metals, and are to be regarded as solid solutions, should not be confused with the true hydrides; e.g., palladium-hydrogen.

32. Cerium Hydride.

If cerium dioxide is reduced by means of metallic magnesium in an atmosphere of hydrogen, the metallic cerium, as fast as it is set free, combines with the gas to form cerium hydride.

Ignite a few grams of ceric ammonium nitrate (No. 171), or cerous ammonium nitrate, at first gently, and finally with the blast lamp, and mix the pure, yellow cerium dioxide thus obtained with powdered magnesium in the proportion of 172 parts CeO_2 to 64 parts Mg. Place the mixture in a boat and introduce it into a short combustion tube, one end of which is connected through a sulphuric acid wash-bottle with a hydrogen generator, while the other end can be closed when required. After the air in the apparatus has been completely replaced by hydrogen, heat the tube in a short combustion furnace, at first gently, until all moisture is removed; then close the exit end of the combustion tube and open the cock of the generator wide so that the reaction mixture stands under a slight pressure of hydrogen. On now heating the tube with the full flame, the mixture glows, the walls of the tube above it become blackened, and gas bubbles pass through the wash-bottle, at first rapidly and then less and less frequently, corresponding to the rate of consumption of the hydrogen. Heat the mixture five or ten minutes longer, and then allow it to cool under hydrogen pressure. The reddish-brown, fairly compact reaction-product consists of a mixture of cerium hydride and magnesium oxide. Break pieces of it from the boat and set fire to them with a match; the material burns with a hydrogen flame to a nearly white ash. While the hydrogen is burning, occasional flashes occur from the ignition of particles of unoxidized magnesium. It is possible to keep cerium hydride for a long time in sealed vessels.

By heating calcium turnings to a dull red heat in an atmosphere of hydrogen, calcium hydride, CaH_2, may be prepared in an analogous manner.

33. Copper Hydride.

From 100 c.c. of a 5% solution of barium hypophosphite (No. 96), precipitate all of the barium by the addition of about 18 c.c. of 2-normal sulphuric acid, and treat the clear filtrate at the room temperature with four grams of copper sulphate dissolved in 15 c.c. of water. After some time, or more quickly if heated to 30°, the solution becomes green, and dark-brown copper hydride is precipitated which to some extent adheres to the sides of the glass vessel as an iridescent film. Filter off the precipitate, wash it with water, and dry the product in a vacuum-desiccator.

Heat a portion of the copper hydride in a small test-tube. It decomposes suddenly into red copper and hydrogen; the latter may be ignited at the mouth of the tube.

Cover a second portion with concentrated hydrochloric acid; hydrogen is evolved, which, in consequence of the admixed spray of copper compounds, burns with a deep-blue flame. From the solution in the test-tube, the addition of a little water precipitates white cuprous chloride.

ACIDS, BASES, AND SALTS.

The majority of the simple compounds are electrolytes, that is, they are acids, bases, or salts. The preparation of simple electrolytes can take place according to the methods outlined on p. 51 as generally applicable for simple compounds; as peculiar to electrolytes, the formation of a compound by the association of its ions, presents a special case of synthesis from the elements. In the preparation of pure electrolytes in solution by bringing together the necessary ions, it is essential that foreign ions should be removed. Thus soluble hydroxides may be prepared by precipitating solutions of the corresponding sulphates with an equivalent amount of barium hydroxide, the barium and sulphate ions being removed as insoluble barium sulphate, and only the desired hydroxide and its ions remaining in solution (cf. No. 36). In a similar way acids may be obtained by the interaction of barium salts and sulphuric acid (No. 33). Potassium iodide, likewise, may be prepared conveniently by the double decomposition of ferrous iodide with potassium carbonate, whereby iron and carbonate ions are precipitated in the form of an insoluble compound (No. 39).

Electrolytic Dissociation is distinguished from simple dissociation by the fact that the products of dissociation are electrically charged. Furthermore, the extent of electrolytic dissociation depends in the highest degree upon the nature of the solvent medium.

$2\,HI = H_2 + I_2$ (non-electrolytic dissociation).
$HI = H^+ + I^-$ (electrolytic dissociation).

This double possibility of dissociation enables substances to react in different ways. According to the first of the above equations, hydrogen iodide is a reducing agent; according to the second, it is an acid.

Electrolytic dissociation can be detected and measured by physical methods, either by estimating the apparent molecular weight of the dissolved substance by one of the osmotic methods, or by determining the conductivity of the solution (Arrhenius); cf. No. 34. As has already been stated in the discussion of the preparation of lithium by the electrolysis of fused lithium chloride (No. 14), the unit of electricity, the electron, can be represented by the symbol ϵ and the process of electrolytic dissociation, or ionization, of a binary compound AB can be represented as follows:

$$AB \rightleftarrows A^+ + B^-$$

which means that neutral molecules of AB have dissociated, or ionized, into positively-charged cations A^+ and negatively-charged anions, B^-. The element A has lost one of its original electrons and thereby obtained a positive charge, the element B has gained an electron and thereby acquired a unit negative.

$$A^0 - \epsilon = A^+; \qquad B^0 + \epsilon = B^-.$$

The same reasoning applies when A or B is a combination of two or more elements. In the original compound, the transfer of an electron from A to B has probably taken place already and a crystal of a salt consists of a rigid lattice of the charged particles, the electrostatic attraction of the opposite charges holding each particle in its definite place so that there can be no movement of the charges and hence no conductivity. Dissolving the salt separates the charged components so that they are no longer held to definite places. Each then possesses its own independent motions and shows the osmotic properties of a complete molecule even although the motion is still restricted in that particles of opposite charge must always be approximately evenly spaced throughout the solution. The application of an outside potential will now draw particles of opposite charge in opposite directions, — in other words, the solution conducts electricity.

Law of Dilution. The application of the law of mass-action to the dissociation of a binary electrolyte gives the following expression:

$$\frac{[\text{cation}]\ [\text{anion}]}{[\text{undissociated compound}]} = k.$$

Thus, in a given case, if the fraction of a gram molecule of a binary electrolyte which has undergone dissociation is denoted by α (the degree of dissociation), then $1 - \alpha$ is the undissociated fraction of the gram molecule which is in undissociated compound is $\frac{1-\alpha}{v}$ and that of each ion is $\frac{\alpha}{v}$. Then according equilibrium with the ions, and at the dilution v the concentration of the to the mass-action law the following relation holds:

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1-\alpha}{v}} = k, \quad \text{or} \quad \frac{\alpha^2}{(1-\alpha)\,v} = k. \quad \text{(Ostwald's Law of Dilution.)}$$

The maximum possible value for α, the degree of dissociation, is 1, and this represents complete dissociation; it is evident that this is approached in proportion as v is made large. Experiment 37 illustrates a case of dissociation with progressive dilution.

Ostwald's dilution law fairly accurately describes the behavior of little ionized acids and bases, but it fails with the highly ionized acids and bases and with salts, which in general are highly ionized. Indeed, De Bye and others hold that salts in solution are 100 per cent ionized and that the apparent lack of complete ionization in concentrated solutions, computed from conductivity and osmotic measurements, is due to certain factors restricting the free motion of the ions.

Ionization Tendency, or Electroaffinity. A measure of the force with which the electron is held to the material atom of an ion is given by the potential which is necessary to effect the discharge of the ion in an electrolysis (decomposition potential). This force is variously known as *ionization tendency* or *electroaffinity.* In the following table, the tension in volts is given which is necessary for the discharge of a few of the metal ions from their normal solutions, on the basis of the discharge-potential of hydrogen being taken arbitrarily as zero.[1]

Mg	+ 1.482	Cd	+ 0.420	Pb	+ 0.151
Al	+ 1.276	Fe	+ 0.344	Cu	− 0.329
Mn	+ 1.075	Co	+ 0.232	Ag	− 0.753
Zn	+ 0.770	Ni	+ 0.228		

In this potential series the distinction which has always been recognized between noble and base metals is again expressed. Elements with a high ionizing tendency possess to a marked degree the ability to form simple ions. Simple ions of the noble metals are less stable, so that the number and importance of the simple salts of these metals is much less than that of their complex salts. (Cf. Chapters IV and V.)

Hydrolytic Dissociation, or Hydrolysis. The formation of a salt by the neutralization of an acid and a base is a reversible process. If M denotes a metal and R an acid radical, then the reaction of equilibrium is:

Neutralization

$$\text{MOH} + \text{HR} \rightleftarrows \text{MR} + \text{H}_2\text{O}$$

Hydrolysis

If the equation is read from right to left it represents an hydrolysis, i.e., the breaking up of a salt into an acid and a base. Neutralization and hydrolysis represent, therefore, reciprocal processes. It is important in the preparation of salts to know which of these reactions preponderates. The mass-action law applied to this reversible reaction gives:

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[1] The choice of an arbitrary zero-point is necessary, since it is only *differences* in potential which can actually be measured.

$$\frac{[HR]\,[MOH]}{[MR]\,[HOH]} = K.$$

Salts, acids, bases, and water are dissociated electrolytically according to the following equations:

$$\begin{aligned}
&1.\ MR &&= M^+ + R^- \\
&2.\ HR &&= H^+ + R^- \\
&3.\ MOH &&= M^+ + OH^- \\
&4.\ HOH &&= H^+ + OH^-
\end{aligned}$$

The corresponding dissociation constants, K_1, K_2, K_3, K_4, may be given as follows:

$$K_1 = \frac{[M^+]\,[R^-]}{[MR]};\quad K_2 = \frac{[H^+]\,[R^-]}{[HR]};\quad K_3 = \frac{[M^+]\,[OH^-]}{[MOH]};\quad K_4 = \frac{[H^+]\,[OH^-]}{[HOH]}.$$

If, in the above equations of hydrolysis, the values for the concentration of undissociated MR, HR, MOH, and HOH obtained respectively from the last four expressions are inserted, the equation

$$K = \frac{K_1 \cdot K_4}{K_2 \cdot K_3}$$

is obtained. This equation expresses all the essential phenomena in neutralization and hydrolysis. It shows that hydrolysis will be greater if the value of K_4 becomes larger; or, in other words, if the temperature is raised, since the dissociation of water, although extremely small, increases quite rapidly with rise of temperature. The hydrolysis is also greater as K_2 and K_3 are smaller, or in other words as the acid and base in question are weaker. Inasmuch as the weakness of the base usually increases with the valence of the metal, it follows that salts of the tervalent metals (Fe, Al, Sb, Bi) are hydrolyzed to a greater extent than the salts of metals having a lower valence (Mn, Ba, etc.) (cf. Nos. 40, 41). The halides of the quadrivalent metals (Sn, Si, Ti) are hydrolyzed to an especially marked extent (cf. Nos. 50 to 52), and it is, therefore, possible to prepare such salts pure only when water is completely excluded. If sulphur chloride is regarded as the sulphur salt of hydrochloric acid (cf. No. 45), this compound then forms the extreme of the hydrolyzable chlorides, inasmuch as the metallic character of the element combined with chlorine has entirely disappeared.

Salts of weak acids and weak bases, such as, for example, the sulphides of aluminium (Nos. 4 and 5) and titanium, can only be prepared when out of contact with water. After they have been prepared synthetically in a crystallized form, they can be kept for some time without change on account of the fact that the velocity at which compact substances enter into reaction is often very slight. (Cf. TiS_2, No. 58.)

If the phosphides, nitrides, and certain carbides are regarded as the metal salts of phosphine, ammonia, and the hydrocarbons, that is to say, as the salts of hydrogen compounds the acid nature of which is almost infinitesimal (the acidic constants, K_2, of which are therefore extremely small), it then becomes easy to understand why these substances can be prepared only in the absence of water (best by direct union of the elements themselves). The readiness with which the preparation of phosphine from calcium or magnesium phosphide (No. 63), of acetylene from calcium carbide (No. 64), and of ammonia from magnesium or boron nitride (Nos. 60, 61), is carried out, depends on the ease with which the salts of such extremely weak acids hydrolyze.

(*a*) *Acids and Bases.*

34. Physico-chemical Detection of Electrolytic Dissociation.

To demonstrate the dissociation of a substance in aqueous solution, determine the molecular weight of nitric acid by the freezing-point method, first with nitrobenzene and then with water as the solvent. Dehydrate some concentrated nitric acid by distilling it with an equal volume of concentrated sulphuric acid, and free the distillate from oxides of nitrogen by passing dry air through it.

Determine the molecular weight by measuring the lowering of the freezing-point of nitrobenzene, using about 25 g. of the solvent, and 0.2, 0.4, 1.0, and 1.5 g. of nitric acid, then repeat, using about 22 g. of water instead of nitrobenzene. The details for carrying out the determinations may be found in H. Biltz; Practical Methods for Determining Molecular Weights, Translated by H. C. Jones, 1899. In nitrobenzene the molecular weight corresponds approximately to the formula HNO_3, whereas in water the molecular weight is about half as large.

In order to show that this dissociation causes the aqueous solution to become a conductor of electricity, insert two platinum electrodes in a beaker of water, and connect them through an electric incandescent lamp with the terminals of a lighting circuit. The lamp does not glow, because water is a very poor conductor of electricity, and the circuit is therefore practically open. As soon, however, as a few drops of nitric acid are added to the water, the lamp begins to glow, and at the same time an evolution of gas takes place at the electrodes.

Test the conductivity of nitrobenzene after the same manner, first alone, and then with the addition of a little anhydrous nitric acid; the lamp does not glow in either case.

35. Hydrobromic Acid. Hydriodic Acid.

(*a*) *From the Elements.* Connect in series, a Kipp hydrogen generator, a wash bottle containing sulphuric acid, a wash bottle containing 80 g. of bromine, and a glass tube about 25 cm. long and 1 cm. wide which is filled for a space of 8 to 12 cm. with loosely-packed, platinized asbestos. (Cf. No. 28.) Place a Bunsen lamp with a flame spreader under the tube. Connect the farther end of the contact tube with a U-tube containing glass beads and moist red phosphorus, then with a wash bottle made from a test tube which contains 1 c.c. of water, and finally with two wash bottles each containing 35 c.c. of water. Keep the latter cooled during the experiment, first with ice-water and later with a mixture of salt and ice.

At the beginning of the experiment, disconnect the train at a point between the contact tube and the phosphorus tube. Fill the apparatus up to this point with hydrogen, then heat the contact layer to faint redness, and when the gas escaping from this tube becomes colorless, reconnect the rest of the apparatus. Regulate the amount of bromine vapor by pouring warm (not hot) water from time to time into the beaker which surrounds the bromine bottle. The gases after passing the contact layer must contain no uncombined bromine, and must therefore be colorless.

From the first receiver fuming hydrobromic acid is obtained, and the yield can be determined by weighing the flask before and after the experiment.

Hydriodic Acid can be prepared from hydrogen and iodine in a similar manner. Dry the hydrogen gas by passing it through three wash bottles containing concentrated sulphuric acid and lead the gas through glass tubing to the bottom of a small fractionating flask which contains 50 g. of iodine and is being heated gently. Insert the short arm of the distilling flask in a cork stopper which fits into a wide glass tube, 70 cm. long, which is also kept warm. Place a plug of platinized asbestos in the wide glass tube not far from the place where the tubing from the flask enters the wider tube, and heat this plug with a wide flame. Any iodine, distilling as such without combining with the hydrogen, will be deposited in the wide part of the tube. Lead the escaping gas mixture into a test tube containing a little water and from thence into two successive small flasks each containing some water. Before starting the experiment, make sure that the entire apparatus is filled with hydrogen, so that there will be no danger of an explosion when the contents of the flask and the platinized asbestos are heated.

(*b*) *By the Intermediate Formation of Phosphorus Bromide.* Provide a 500 c.c. flask with a stopper and dropping funnel and connect it by means of delivery tubing with two U-tubes placed in series. From the last U-tube carry a bent delivery tube through a tight-fitting cork well towards the bottom of a flask which is to serve as a receiving vessel. Provide this flask with an exit tube starting from just inside the cork and bending downward externally so as to nearly reach the surface of some water placed in another flask. Do not, during the process which follows, allow the tube entering either of the last-mentioned flasks to dip beneath the surface of the solution contained in them.

Place in the evolution flask, first a layer of 25 g. sand, then upon this a mixture of 100 g. sand and 25 g. red phosphorus, and moisten the whole with 45 c.c. water. Fill the first U-tube with glass beads, the second with glass beads mixed with moist red phosphorus, and in the receiving flask place 80 c.c. of water. The delivery tube which enters the receiver must reach only to a point just above the surface of the liquid, since if it dipped into the solution, the latter might be sucked back into the evolution flask.

Wrap the evolution flask in a towel, because it sometimes breaks at the beginning of the experiment; cool the first U-tube with a mixture of salt and ice, and the receiver with ice. Introduce from the funnel 200 g. bromine, drop by drop, into the mixture of sand and phosphorus. At the beginning of the reaction cool the evolution flask by placing it in a dish containing cold water. Yield, about 250 g. of concentrated hydrobromic acid, which is collected in the first receiving flask. Determine its density by means of a Westphal balance. Hydrobromic acid can also be prepared from bromine and hydrogen sulphide. (Cf. A. Recoura, Compt. rend. **110**, 784 (1890)). Dependent preparations: Cupric Bromide (No. 37), Ammonium Tribromide (No. 69), Hexammine Nickelous Bromide (No. 128), Praseocobalt Bromide (No. 135).

36. Thallous and Thallic Hydroxides.

Thallium in thallous halides and in thallous sulphide shows unmistakable similarity to silver and lead: in thallous hydroxide and in the thallous double salts, it appears like an alkali metal. In the tervalent thallic compounds, thallium is similar to aluminium quite in accordance with its position in the periodic classification.

Mix 13.3 g. of thallous nitrate[1] (1/20 mol.) and 3 g. concentrated sulphuric acid in a platinum crucible, and drive off the volatile acid slowly by heating the upper edge of the crucible with a Bunsen burner which is held in the hand and moved about so as to avoid spattering. The decomposition is complete when the contents of the crucible no longer give off acid vapors. Dissolve the thallous sulphate thus prepared in 50 c.c. of water, and precipitate barium sulphate from the boiling solution by adding a hot solution of 8 g. crystallized barium hydroxide, the amount of the latter reagent being slightly in excess of that theoretically required. After filtering, precipitate the excess of barium hydroxide by the careful addition of very dilute sulphuric acid. A drop of the solution should not, at the last, give a precipitate either with barium hydroxide or with sulphuric acid. Evaporate the solution to a volume of about 25 c.c., filter again and then evaporate to about 5 c.c., after which, place the evaporating dish in a desiccator over dry lime. Suck the crystals of thallous hydroxide free from liquid in a small filter funnel and obtain a second crop by further evaporation of the mother liquor. Neutralize the last mother liquor with nitric acid, and use the resulting solution of thallous nitrate for the reaction described below.

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[1] In order to obtain thallous nitrate from metallic thallium, cut the latter into small pieces and dissolve them in the calculated amount of dilute nitric acid. Introduce hydrogen sulphide into the hot, slightly acid solution to remove lead as sulphide, and evaporate the filtrate until the nitrate crystallizes out. Drain the crystals with suction, and evaporate the mother liquor together with the wash-water for more crystals. Yield, theoretical. F. Foerster (Z. anorg. Chem. **15**, 71 (1897)) shows how thallium can be recovered from the flue gas of pyrite burners.

Thallous hydroxide forms light-yellow crystals which are readily soluble in water; the aqueous solution of these crystals is strongly alkaline, its electrical conductivity being nearly the same as that of a sodium hydroxide solution of the same concentration. Filter paper moistened with thallous hydroxide serves as a reagent for detecting the presence of ozone; brown thallic oxide is formed.

Reactions of Thallous Salts. Solutions of thallous salts when treated with iodide solutions give a yellow, very difficultly soluble precipitate of thallous iodide (analogous to AgI); with chloroplatinic acid, they give light-yellow, difficultly-soluble thallium chloroplatinate, $Tl_2[PtCl_6]$ (analogous to $K_2[PtCl_6]$); with ammonium sulphide, or hydrogen sulphide together with sodium acetate, they give a deep-brown precipitate of thallous sulphide (analogous to Ag_2S).

Hydrated Thallic Oxide (analogous to hydrated ferric oxide). Oxidize a part of the thallous nitrate solution by the addition of an excess of bromine, and precipitate the resulting brown solution by adding concentrated ammonia. The very fine precipitate settles slowly. Wash it by decantation with water containing ammonia until the decanted liquid is free from bromine, and then drain it upon a filter. Dry the product in a desiccator over sulphuric acid, for at higher temperature it loses water and becomes thallic oxide.

Thallic Thallous Chloride, $TlCl_3 \cdot 3\,TlCl$. Dissolve a small quantity of hydrated thallic oxide, or the anhydrous oxide, in a little hydrochloric acid, dilute with about one-third of a test-tubeful of water, an equal volume of normal oxalic acid solution and boil, whereby carbon dioxide will escape. After heating a few minutes, allow the contents of the test tube to cool: iridescent small crystalline flakes of the above-named salt will be deposited.

(b) *Halogen Compounds.*

37. Cupric and Cuprous Bromides.

Dissolve 16 g. of cupric oxide in a solution of hydrobromic acid containing 33 g. of pure HBr. Filter the resulting solution and evaporate it to a small volume, whereby the color becomes very dark. Place the evaporating dish, with its contents, in a desiccator over sulphuric acid, preferably in a vacuum; an almost solid mass of crystals forms in a few days. Break up this mass thoroughly once each day to accelerate the drying process. Cupric bromide is of a deep-black color and glistens somewhat like iodine.

Heat a portion of the cupric bromide cautiously in an evaporating dish; it loses bromine and is changed into white cuprous bromide. Cuprous bromide is practically insoluble in water.

The color of the cupric bromide solution varies with the dilution; the most dilute solutions, which contain practically all the copper in the state of the simple ions, are light blue; the most concentrated ones have a dark-brown color from non-ionized cupric bromide and complex ions; other concentrations have intermediate shades.[1]

38. Cuprous Chloride.

Treat 50 g. crystallized cupric sulphate and 25 g. sodium chloride (or 37 g. crystallized cupric chloride) in a flask with 150 g. concentrated hydrochloric acid and 20 g. copper turnings. Heat upon the water bath until, at the end of about an hour, the green color has disappeared. Pour the clear solution into a liter of water containing a little sulphurous acid, whereby white cuprous chloride, insoluble in dilute hydrochloric acid, is precipitated. Wash the precipitate by decantation with water containing sulphurous acid, finally drain it with suction and wash successively with glacial acetic acid, alcohol, and ether. Dry it in the hot closet. Yield, about 20 g.

39. Potassium Iodide. Iodine from Iodide Residues.

By the action of iodine upon a caustic potash solution, a mixture of potassium iodide and iodate is produced, and this can be reduced completely to the iodide by heating with charcoal. By extracting the mass with water and recrystallizing, the product can be purified.[2] Potassium iodide can also be prepared without the intermediate formation of iodate, by the interaction of ferrous iodide (which can be obtained synthetically from the elements) and potassium carbonate.

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[1] The light-blue color of the dilute solutions is the characteristic color of all solutions of cupric ions. The changes in color with increasing concentration may be due, certainly in part, to an increasing proportion of undissociated molecules, but it is also quite certain that changes in the state of hydration of the dissolved salt have a large influence in altering the color.

[2] Cf. Preparation of potassium bromate and bromide, No. 78.

Shake 7 or 8 g. iron filings and 50 c.c. water in an Erlenmeyer flask with 25 g. iodine added in small portions. Warm the mixture somewhat until all of the iodine has combined, and the color of the solution has become deep yellow (ferrous iodide); then pour off the liquid from the excess of iron. Add five grams more of iodine to the solution and heat until it is dissolved.[1] Pour this solution into a boiling solution of 17 g. potassium carbonate in 50 c.c. water. The mixture, which at first is very thick, becomes more fluid upon further heating, since the precipitate assumes a more compact form. A little of the solution when filtered must be perfectly colorless, and free from iron; if this is not the case, add a little more potassium carbonate to the boiling solution. Evaporate the filtrate to a small volume in a porcelain dish, filter again, and evaporate further in a beaker until crystals begin to separate. Then allow the solution to evaporate slowly by placing the beaker in a warm place (as on top of the hot closet). Drain the crystals in a funnel, wash them with a little cold water, and save the mother liquor for another crop of crystals. Yield, 25 to 35 g.

The potassium iodide when dissolved in a little water and acidified should not show any yellow color (free iodine), which would indicate the presence of iodate in the salt. Dependent preparation: Potassium lead iodide, No. 106.

Iodide residues, such as result from chemical work in organic laboratories, can be easily worked up into iodine by oxidation with oxygen gas in acid solution, with oxides of nitrogen as catalyzer. Half fill a 5-liter flask with the solution of iodide residues and fit the flask with a stopper carrying a glass tube which reaches down to about the middle of the flask. Make the solution strongly acid with commercial sulphuric acid, which should heat the mixture somewhat. With the flask loosely stoppered, introduce oxygen gas until the air has all been replaced, then add a little concentrated sodium nitrite solution and insert the stopper tightly into the neck of the flask. To prevent any difficulty from the liquid backing up into the gas-delivery tubing, it is well to provide an empty gas-washing flask. On shaking the contents of the large bottle, an energetic reaction takes place and there is a noticeable consumption of oxygen. Shake, at first carefully, then more strongly and continuously. When there is no more consumption of oxygen, raise the stopper a little, fill the flask with fresh oxygen, add a little more sodium nitrite solution and repeat the operation. Continue until there is no further evidence of any consumption of oxygen. Allow the iodine to settle out in the bottom of the flask, pour off the supernatant liquid, which is usually colorless, wash the residue with a little water and filter off the crude iodine.

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[1] The extra addition of the iodine serves to partially oxidize the ferrous salt, and the subsequent precipitate thus contains hydrated ferric oxide and is readily filtered; ferrous carbonate would be very difficult to filter.

Purify the product by distillation with steam. It is best to avoid the use of a water-cooled condenser. Lead the vapor of steam and iodine into the middle of a large Erlenmeyer flask. The stopper of this flask should contain two holes, one to receive the tube through which the vapors enter and the other a tube extending about half a meter upwards, to serve as an air condenser. Clamp the flask in a dish containing cold, running water.

Filter off the purified iodine, drain it with suction and dry in a vacuum desiccator over calcium chloride. It requires a long time to accomplish a thorough drying of the iodine in this way. It is quicker to heat the iodine on the water bath in an evaporating dish, which is covered with a watch glass. Iodine and some water will collect on the watch glass. After some minutes, replace the watch glass with another one, and scrape off the iodine on it. When the condensate on the watch glass appears to be iodine without any drops of water, the iodine is practically dry.

To further purify the iodine, place it in a large beaker, cover the beaker with a Kjeldahl flask filled with cold water, and heat the bottom of the beaker so that the iodine sublimes and collects on the flask.

40. Barium Chloride from Witherite.

If a sample of witherite is dissolved in hydrochloric acid, the resulting solution of barium chloride contains iron as well as other impurities. The simplest way to remove the iron is to oxidize it with a little chlorine water, and then precipitate it by adding an excess of the powdered mineral (cf. the barium carbonate method for the analytical separation of metals, the salts of which hydrolyze to different degrees; see p. 68). The more difficultly soluble barium chloride is freed from any calcium and strontium chlorides by crystallization.

First determine with a Westphal balance the density of the pure, concentrated hydrochloric acid which is to be used, find the percentage of HCl by referring to specific gravity tables, and compute the volume of the acid required to dissolve 100 g. of witherite. Place this amount in a two-liter flask, dilute it with water to a volume of 1500 c.c., add the powdered witherite and heat until the mineral is dissolved. Impurities such as silicates may remain as insoluble residue. Add 50 c.c. of chlorine water, then 5 to 10 g. more of witherite, and allow the solution to stand in a warm place with frequent shaking. Next morning again add from 2 to 5 g. of witherite. From time to time filter a little of the solution and test with potassium thiocyanate for iron. When all the iron has been precipitated, filter, and evaporate the filtrate until crystallization takes place. If during the evaporation any more ferric hydroxide, which may have been held in colloidal solution, separates, filter it off after the volume has been reduced to one-half. Finally, drain the crystals of barium chloride in a funnel and concentrate the mother liquor for more crystals. Redissolve all the crystals in water, acidify with a few drops of hydrochloric acid, filter and recrystallize. Yield, 100 to 110 g. of $BaCl_2 \cdot 2\,H_2O$.

41. Manganous Chloride from Waste Manganese Liquors.

Pure manganous chloride can be obtained by crystallizing the waste liquor obtained in the preparation of chlorine from pyrolusite and hydrochloric acid, if, as in the last preparation, the iron is first removed.

Similarly, the waste liquor from hydrogen generators can be freed from iron and worked up into pure zinc salts.

Evaporate 2 to 3 liters of the manganese liquor in a porcelain dish over the free flame in order to expel the excess of hydrochloric acid. Dissolve the residue, which solidifies on cooling, in 3 to 4 liters of water. Dilute one-tenth of this solution in a flask with a large amount of water, and add caustic soda, avoiding an excess, in order to precipitate manganese hydroxide. After settling, siphon off the clear solution, shake up the precipitate with pure water, and wash it repeatedly by decantation until, at the end of three or four days, all of the sodium salt has been removed. Add the manganese slime thus obtained to the remaining nine-tenths of the first solution, and allow the mixture to stand for several days in a thick-walled, five-liter flask which is placed in a warm place. Shake the mixture frequently until all of the iron has been precipitated by means of the manganese hydroxide. This usually requires about two days, and at the end a little of the filtered solution should give no test with potassium thiocyanate. Filter the solution through a plaited filter and evaporate it until crystals begin to separate. Then transfer it to a flask and cool rapidly while rotating under the water tap. Drain the crystal meal in a suction-funnel and wash it first with 50%, and then with pure alcohol. By evaporating the mother liquor a further yield is obtained. Allow the light pink crystals, which are still moist with alcohol, to dry in contact with the air.

42. Anhydrous Ferric Chloride; Preparation of Chlorine.

Clamp a tubulated retort (cf. Fig. 15, p. 78), of about 250 c.c. capacity so that its neck (which is 1 to 2 centimeters wide) is in a horizontal position. Insert a bundle of iron wires (about 0.1 cm. in diameter), weighing 10 to 25 g., to about the middle of the neck, and connect the end of the latter, through two sulphuric acid wash-bottles, with a chlorine generator. Into the tubulus of the retort insert a vertical tube, about 50 cm. long and 1 cm. wide, making the joint tight by means of a short piece of rubber tube. Place the whole apparatus under the hood.

Conduct a fairly rapid stream of chlorine into the retort, and heat gently, with a small flame that does not touch the glass, that part of the neck which contains the iron wire. Very soon a reaction begins to take place with the emission of light, and a shower of brilliant, glistening leaflets falls into the bulb of the retort. Heat the neck of the retort by fanning it with a second and larger flame until all of the ferric chloride is sublimed into the bulb. Tap the vertical tube lightly so that any of the product condensed in it will fall back into the retort.

At the end of the experiment shake the product, which is very hygroscopic, directly from the retort into a dry, wide-mouthed, glass-stoppered bottle. The preparation keeps well if the stopper is made air tight with a little vaseline.

Preparation of Chlorine.

Large quantities of chlorine may be prepared by the oxidation of hydrochloric acid with pyrolusite. Half fill a round-bottomed flask of from 1.5 to 2 liters capacity (cf. Fig. 14, p. 77F) with lumps of pyrolusite, and close the flask with a two-holed stopper;[1] through one hole insert a thistle tube, which serves as a safety tube, and must extend 20 to 30 cm. above the top of the flask and nearly to the bottom inside. Through the other hole insert a short delivery tube bent at a right angle. To cause the evolution of chlorine, pour concentrated commercial hydrochloric acid through the thistle tube until the pyrolusite is just covered, and heat the mixture gently on a Babo funnel; regulate the rate at which the gas is generated by altering the height of the flame under the evolution flask. A single charge of pyrolusite is sufficient to react with several refillings of the acid. Wash the gas with water, and dry it (if necessary) by passing it through one or two bottles containing concentrated sulphuric acid.

It is very convenient to use the dry liquid chlorine which can be purchased in steel cylinders under pressure; but this is only to be recommended when large amounts are frequently used.

When it is desired to prepare a definite amount of chlorine, an excess of hydrochloric acid can be decomposed by means of a weighed quantity of potassium permanganate or of potassium pyrochromate.

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[1] Cork stoppers can be made air tight by immersing them in molten paraffin at about 150°. Such a paraffined stopper should be tightly wired in place to prevent it from popping out when the flask is heated.

$$2\ KMnO_4 + 16\ HCl = 2\ MnCl_2 + 2\ KCl + 8\ H_2O + 5\ Cl_2,$$
$$K_2Cr_2O_7 + 14\ HCl = 2\ CrCl_3 + 2\ KCl + 7\ H_2O + 3\ Cl_2.$$

43. Anhydrous Ferrous Chloride; Preparation of Hydrogen Chloride.

On account of its higher melting-point it is more difficult to prepare anhydrous ferrous chloride than the corresponding ferric salt. Clamp a porcelain tube, 50 to 60 cm. long and 3 cm. in inside diameter, in a horizontal position under the hood. Adjust it at a suitable height above the blast lamp, and surround it with an asbestos heating chamber (Fig. 4, p. 3). Introduce a loose bundle of iron wires (0.1 cm. in diameter), weighing from 12 to 15 g., into the part of the tube which can be heated hottest. Conduct into the tube a rapid current of hydrogen chloride gas (see below) which is produced by the action of concentrated, commercial sulphuric acid upon 750 c.c. of concentrated, commercial hydrochloric acid. Place a beaker in a tilted position over the open end of the tube. Maintain the temperature as high as possible during the experiment. The product condenses in the cooler parts of the tube, and to some extent in the beaker.

The yield is 15 to 20 g. of dirty-white, hygroscopic, leaf-like crystals.

Small amounts of ferrous chloride can be prepared in a similar way in a wide combustion tube which is heated in a furnace.

Aluminium chloride can be prepared in like manner from aluminium and hydrogen chloride.

Preparation of Hydrogen Chloride.

Small amounts of hydrogen chloride are most conveniently prepared in a Kipp generator containing large pieces of sal ammoniac (ammonium chloride) upon which concentrated sulphuric acid is allowed to act. This method does not work as well for preparing large quantities of the gas, because the foaming which occurs becomes troublesome.

Larger amounts of hydrogen chloride may be obtained by treating 200 g. common salt (sodium chloride) with a cooled mixture of 320 g. sulphuric acid and 80 g. water in a round-bottomed flask, which may be conveniently heated upon a Babo boiling funnel. On cooling, the flow of the gas slackens, but it can be started again by renewed heating. When the mixture has become exhausted, it should be poured out of the flask while still warm, since on cooling it becomes solid, and is then difficult to remove. But it must be poured into a dry receptacle to avoid an explosive formation of steam.

The following method, which depends upon the fact that hydrogen chloride is but slightly soluble in concentrated sulphuric acid, is also to be recommended.[1] Allow concentrated sulphuric acid to drop from a dropping funnel into a large suction flask containing concentrated hydrochloric acid, to which a handful of common salt may with advantage be added. It is advisable to let the sulphuric acid fall first into a small test-tube so that by its flowing uniformly over the edge of the latter a steady evolution of gas is produced. The rate of flow of gas from the flask is governed by the stopcock which regulates the dropping of the sulphuric acid.

The reverse process of adding hydrochloric acid to concentrated sulphuric acid may also be used, but in order to make the lighter hydrochloric acid solution mix thoroughly with the heavier sulphuric acid it is necessary to draw out the stem of the dropping funnel into a capillary which reaches nearly to the bottom of the generating flask.

44. Anhydrous Chromium Trichloride.

Place 10 to 20 g. of coarsely powdered, metallic chromium (No. 3) in an apparatus constructed like that used in the last preparation. Expel the air completely by means of a stream of *dry* chlorine, which will take at least half an hour, and then heat the metal in a current of perfectly dry chlorine for from thirty minutes to an hour at as high a temperature as possible. After cooling, replace the chlorine by carbon dioxide and shake the preparation out of the tube. Beautiful, glistening, violet flakes are obtained, together with a darker powder of a more brownish shade which under the microscope is shown to be crystalline. Collect the two forms separately. Chromium trichloride is, on account of its slow rate of solution, practically insoluble in water.

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[1] The same method may be used for the production of sulphur dioxide if concentrated sulphuric acid is allowed to drop into a solution of commercial sodium bisulphite.

It is difficult to clean the porcelain tube after this experiment. Stopper it at one end, and fill it with commercial, concentrated hydrochloric acid to which a little ferrous sulphate has been added, and let it stand. Dependent preparations: Chromium Nitride (No. 62), Hexamminechromic Nitrate and Chloropentamminechromic Chloride (No. 140).

45. Sulphur Chloride, S_2Cl_2.

Of the chlorides of sulphur, S_2Cl_2 is the only one stable at the laboratory temperature. The chloride SCl_4 is a yellowish-white substance which melts at $-30°$ and decomposes at a few degrees above the melting-point. The dark red compound SCl_2 exists in mixtures of S_2Cl_2 and Cl_2.

Connect a tubulated retort (Fig. 14) of 250 c.c. capacity with a condenser, an adapter, and a suction flask which serves as a receiver; from the side arm of the latter, lead a glass tube to the ventilating flue. Fill the retort with 100 g. of flowers of sulphur, and heat it upon a Babo funnel, or, better still, in a nickel air-bath, to a temperature of from 200° to 250°. Conduct into the retort a rapid current of chlorine, which has been washed once with water and once with sulphuric acid. The sulphur chloride that is formed distils completely into the receiver; a slight blackish coating which remains behind is due to impurities in the sulphur. The operation requires about four hours.

To the crude product thus prepared, add 10 to 15 g. of sulphur which combines with the excess of chlorine. Distil the sulphur chloride from a fractionating flask provided with a condenser and a receiver, and if more than a small amount passes over before a temperature of 130° is reached, pour it back into the flask and add more sulphur. Then distil again, rejecting the portion that passes over below 134°, and collecting as pure product the distillate between 137° and 138°. Only towards the end of the process does the temperature rise a few degrees above this point, due to superheating of the vapors. The excess of sulphur remains behind in the flask. The preparation may be further purified by another fractionation. The yield is almost theoretical.

Sulphur chloride, S_2Cl_2, as ordinarily obtained, is a yellowish-red, heavy liquid which fumes a little in the air, has an unpleasant odor, and attacks the mucous membrane. When distilled in vacuum it has a pure yellow color. This preparation should be carried out in a room reserved especially for working with noxious compounds, and the liquids should be transferred from one vessel to another only when under the hood.

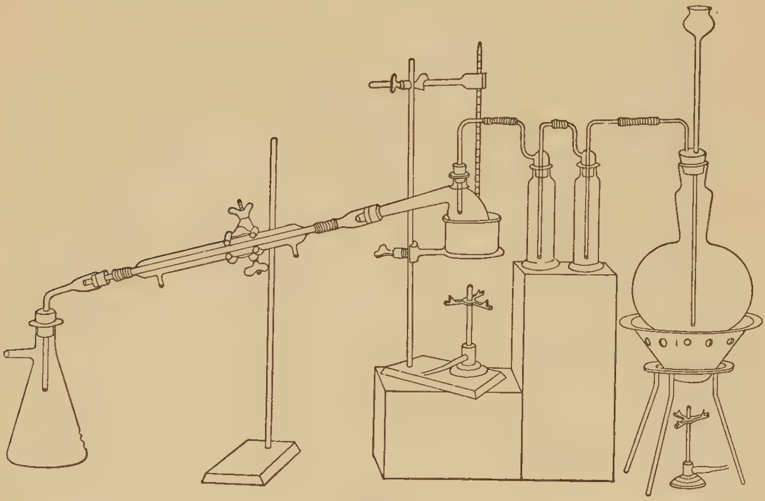

Fig. 14

46. Chlorides of Phosphorus.

Chlorine combines with phosphorus to form either the liquid trichloride or the solid pentachloride according to whether the phosphorus or chlorine is present in excess. Phosphorus trichloride boils undecomposed at 76° C.; on heating phosphorus pentachloride, it vaporizes without passing through the liquid phase. Density determinations of the gas show that the pentachloride is appreciably dissociated at 180°, and practically completely so at temperatures above 290°, into phosphorus trichloride and chlorine; the latter can be identified by its yellowish-green color. On cooling, the dissociation products recombine and again form the pentachloride.

Phosphorus oxychloride is most conveniently prepared by oxidizing phosphorus trichloride with potassium chlorate.

$$3\,PCl_3 + KClO_3 = 3\,POCl_3 + KCl.$$

Phosphorus Trichloride. Use the same apparatus as in the preparation of sulphur chloride (No. 45), except that the heating bath under the retort is in this case superfluous. Cut 31 g. of yellow phosphorus under water in a porcelain mortar into pieces which are not too small. Take the pieces out with pincers, dry them by rapidly pressing between filter papers and introduce them through the tubulus into the retort which has previously been filled with carbon dioxide gas. Avoid handling the phosphorus with the fingers, because it takes fire easily, and phosphorus burns are severe and frequently dangerous. Any residue of phosphorus left in the mortar should be wiped out with moist filter paper, and the paper immediately burned.

On conducting chlorine into the retort, the phosphorus ignites, melts, and burns with a pale flame to phosphorus trichloride. Outside heating of the retort is unnecessary, but it is important to have the stream of chlorine pass rapidly and steadily. Regulate the reaction from time to time, as necessary, by raising or lowering the tube through which the chlorine enters the retort; this tube should be fitted so that it can be moved readily. Lower the tube if a white sublimate of phosphorus pentachloride forms in the upper part of the neck of the retort; raise it a little if a yellowish-red sublimate begins to make the neck of the retort opaque. This regulation, which is necessary for the proper carrying out of the experiment, does not involve any difficulty.

Purify the crude product by distilling it from a flask with a side-arm condenser (Fig. 7, p. 6). Boiling-point, 76°. Yield, 100 to 120 g.

Phosphorus Pentachloride. Close a wide-mouthed liter bottle by means of a three-holed cork. Through one hole introduce the stem of a dropping funnel so that it reaches just inside the stopper; through the second hole insert a glass tube of 1 cm. bore which reaches to the middle of the bottle and serves for the introduction of chlorine; through the third hole insert another tube which ends just below the cork and serves for the escape of the excess of chlorine. Provide the 1 cm. wide vertical tube with a side arm through which the chlorine is to be introduced, and close the upper end with a cork stopper. Then when the lower part of the tube becomes clogged with phosphorus pentachloride, it is only necessary to remove the stopper a moment and push the obstruction out of the way with a stirring rod.

Conduct chlorine into the flask, and at the same time introduce phosphorus trichloride through the dropping funnel; the two substances immediately combine. Care should be taken to keep chlorine present in excess. At the end loosen the phosphorus pentachloride formed by means of a spatula, and allow the flask, which is still filled with chlorine, to stand for some time before removing the product. The yield is almost quantitative. Dependent preparation: Thionyl Chloride, No. 151.

Phosphorus Oxychloride. Connect a 150 to 200 c.c. distilling flask, containing 21 g. (one-sixth mol.) of finely powdered potassium chlorate, with a condenser and receiver. Then allow 69 g. of phosphorus trichloride (one-half mol.) to flow into the flask a little at a time. After each addition of the chloride, wait until the reaction, which is made evident by a gentle ebullition, has ceased before adding more; at the start it is permissible to warm slightly if necessary. Should a little liquid distil over into the receiver during this operation, return it to the distilling flask.

When the reaction is complete, distil the phosphorus oxychloride by heating with a large flame, holding the burner in the hand and playing the flame around the bulb of the flask. A thermometer is not necessary for this distillation. Clean and dry the apparatus, and redistil the product, this time using a thermometer. Collect the first few drops which come over separately. Boiling-point, 110°. Dependent preparation: Triethyl Phosphate, No. 157.

47. Chlorides of Antimony.

Antimony Trichloride. Treat 100 g. of finely powdered stibnite, in a 750 c.c. flask, with 400 g. of concentrated, commercial hydrochloric acid, shaking frequently and heating upon the water bath until as much as possible of the material is dissolved. Boil the solution five minutes in order to remove the greater part of the dissolved hydrogen sulphide. Add five cubic centimeters more of concentrated hydrochloric acid, and filter the solution through a Büchner funnel containing a layer of asbestos-felt which has been previously moistened with the concentrated acid.

Distil the antimony trichloride solution from a retort, provided with a thermometer, until the temperature reaches 120°; in order to prevent bumping, place bits of pumice or of unglazed porcelain in the liquid. The distillate consists chiefly of hydrochloric acid, containing eventually some arsenic trichloride.

Transfer the liquid remaining in the retort, after again filtering through asbestos if necessary, to a distilling flask. Fit the side arm of the latter by means of a cork stopper to a long tube about 1 cm. in diameter which serves as a condenser (cf. Fig. 8, p. 7). The distillate first passing over is clear, then becomes more or less yellowish due to ferric chloride, and finally, when the temperature is above 215°, it becomes colorless again. At this point change the receiver for a dry, clean, weighed Erlenmeyer flask. The last portion of the distillate solidifies, on cooling, into a radiating mass of crystals. It can be further purified by redistillation. Boiling-point, 223°.

Pour the first fraction of the distillate, which consists of a mixture of hydrochloric acid and antimony trichloride, into a large quantity of water; collect the precipitated basic antimony chloride (essentially a mixture of $SbOCl$ and Sb_2O_3) on a filter and wash and dry it. Dependent preparation: Metallic Antimony, No. 7.

Antimony Pentachloride. Pass dry chlorine gas into fused antimony trichloride until the gain in weight corresponds to that required for the change to the pentachloride. At first the reaction mixture must be kept above the melting-point of pure trichloride, but as more and more of the pentachloride, which is liquid under ordinary conditions, forms, the mixture may be allowed to cool to room temperature. Concerning the preparation of the beautifully-crystalline salicylic acid methyl ester of antimony pentachloride, $C_6H_4(OSbCl_4)CO_2CH_3$, see A. Rosenheim and W. Loewenstamm, Ber. **35**, 1126 (1902).

48. Iodides of Bismuth.

Bismuth Tri-iodide. Triturate 8 g. of sifted, powdered bismuth with 13 g. of iodine in a mortar, and introduce the mixture into a 50 c.c. plain retort. Cut off the neck of the retort to a length of about 7 cm., and suspend the whole with a loop or spiral of wire from a ring-stand in such a way that all portions of the retort can be heated freely. On heating the mixture a feeble reaction is soon observed. On heating more strongly, a little iodine sublimes at first, and should be driven off by playing a second flame over the neck of the retort (Hood); then the bismuth tri-iodide sublimes and condenses in the form of a shower of crystalline spangles. Collect these in a porcelain evaporating dish which is placed so that the neck of the retort rests in its lip. Cover the dish with a watch-glass, and protect the space still left open with some asbestos paper cut to the proper shape.

On standing, bismuth iodide decomposes rather easily with liberation of iodine.

Basic Bismuth Iodide, BiOI. Triturate 10 g. of bismuth tri-iodide in a mortar with water, and decant off the liquid together with the finest powder into a beaker; treat the residue with another portion of water in exactly the same way, and continue the treatment until all of the material is obtained in a state of finest subdivision with from 200 to 400 c.c. of water. Boil the mixture for an hour or two, collect the product of hydrolysis on a suction filter, wash it with water, and dry it in the hot closet. Small, light-brown to red crystal leaflets are obtained which are somewhat lighter colored than red phosphorus. Yield, about 7.5 g.

The hydrolysis of the iodide, which is difficultly soluble in water, takes place more slowly than that of the more soluble chloride, an indication that such interactions of a solid substance under a liquid do not take place with the solid itself, but involve rather only that part of the substance which exists, at the moment, in solution.

49. Bismuth Tribromide.

A mixture of powdered bismuth and bromine reacts only slowly and incompletely in the cold, but with almost explosive violence when heated. The simplest way to prepare bismuth tribromide is to pass bromine vapors over heated bismuth.

The apparatus employed is similar to that used in the preparation of ferric chloride (No. 42). The neck of a tubulated retort, of from 100 to 150 c.c. capacity, is bent downward a little, near the bulb, and a little farther away it is bent upward (cf. Fig. 15). Introduce 10 to 15 g. of bismuth in the depression of the neck, and connect the end of the latter with a wash bottle containing bromine, through which dry carbon dioxide is to be passed in the direction of the retort.[1] Through the tubulus of the retort introduce a glass tube one-half meter long and about 1 cm. in diameter, and make the joint tight with a piece of rubber tubing around the glass. This long tube is to serve as a condenser, and to lead the excess of bromine into the hood.

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[1] Instead of conducting bromine diluted with carbon dioxide over the bismuth, the pure vapors may be distilled from a second smaller retort. The reaction then takes place more rapidly, but requires more attention.

After starting the current of carbon dioxide, heat the bismuth gently by means of a Bunsen burner with a flame spreader, and warm the bromine by placing the wash bottle in warm water and renewing the latter as it cools. Dark-red vapors of bismuth bromide form and condense as yellow flakes in the bulb of the retort, and to some extent in the glass tube.

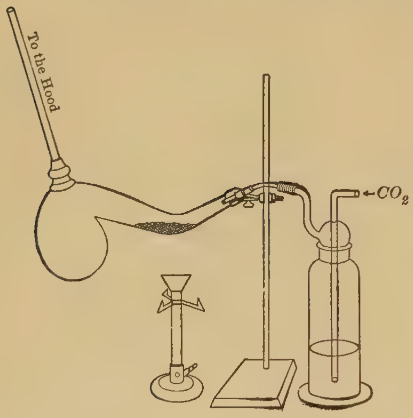

Fig. 15.

Break the retort, collect the product, and let it stand over night in a vacuum desiccator to remove any adhering bromine; or, distil it from a smaller plain retort. The neck of the latter should be about 8 cm. long and the whole should be suspended in a double loop of wire (cf. No. 48). Yield, nearly theoretical.

Boiling-point of Bismuth Bromide. Use a thermometer filled under pressure, which measures temperatures as high as 540°.[1] Place the bismuth bromide in a Jena glass test-tube, 20 cm. long and 2.5 cm. wide, and heat until the substance boils; suspend the thermometer so that it reaches well into the vapor. When the vapors first begin to reach the mercury bulb, lower or remove the flame for a while so as to avoid heating the thermometer too suddenly; then heat strongly again. Correct the boiling-point as thus determined either as directed in No. 6, or by means of finding the apparent boiling-point of pure sulphur under exactly the same conditions. The difference between the latter observed reading and 448° (the true boiling-point of sulphur) is to be applied as a correction to the apparent boiling-point of the bismuth tribromide. This very simple method of making the correction for stem exposure gives good results, provided the two temperatures compared are not far from one another. Boiling-point of bismuth bromide, 466°.[1]

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[1] Cf. No. 54 for the thermoelectric measurement of temperatures.

50. Tin Tetrachloride.

Make use of the same apparatus as described under the preparation of sulphur chloride (Fig. 14, p. 77F). Place 60 g. of tin in the retort, and heat it by placing a Bunsen flame underneath. After the tin is melted pass a rapid current of chlorine, allowing it to play directly on the surface of the metal. Liquid tin tetrachloride, which is colored yellow by dissolved chlorine, collects in the receiver. When the metal in the retort has all disappeared, add some tinfoil to the distillate in the receiving flask, stopper the latter, and allow it to stand until the next day in order that the dissolved chlorine may all react with the tin.

Place the crude product together with a little tinfoil in a 100 c.c. distilling flask, provided with a side-arm condenser (Fig. 7). Fit a thermometer in the neck of the flask, and distil the liquid at the hood, rejecting the first few drops which pass over. If the distillate is not perfectly colorless, allow it to stand over night with more tinfoil and repeat the distillation. Boiling-point, 113.5° to 114°. Preserve the preparation in a sealed vessel.

When exposed to the atmosphere, tin tetrachloride absorbs water and soon becomes changed to the solid white hydrate. Tin tetrachloride can, like titanium tetrachloride, be transformed into the corresponding sulphide (cf. Titanium Disulphide, No. 58). The formation of colloidal stannic acid from tin tetrachloride is discussed under Purple of Cassius, No. 25.

A very convenient method for making tin tetrachloride at room temperatures from tin and dry chlorine has been described by R. Lorenz.[2] Fill a test tube, about 4 cm. wide and 40 mm. long, about one-quarter full of dry granulated ~~zinc~~ tin. Place a cork in the tube, carrying tubing for the introduction of dry chlorine and also for the escape of gas. Fasten the tube in an upright position and introduce chlorine with the tube reaching nearly to the bottom of the test tube. At first introduce the gas slowly, and later, when liquid stannic chloride has formed, increase the rate of flow.

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[1] Author's observation: Victor Meyer found 453° with an air thermometer. Ann. **264**, 122 (1891).

[2] R. Lorenz, Z. anorg. Chem., **10**, 44 (1895).

From time to time raise the tubing through which the gas is flowing but never let it reach above the top of the liquid chloride. Purify the stannic chloride as described above.

This method of preparation corresponds to the method used technically for the recovery of tin from waste tin plate.

51. Silicon Tetrachloride.

For preparing silicon tetrachloride from the elements, either commercial silicon obtained in the electric furnace, or the crystallized product prepared by the thermite process (No. 4), may be used.

Generate chlorine in a two-liter (or larger) flask from pyrolusite and concentrated hydrochloric acid, and wash the gas once with water and twice with concentrated sulphuric acid. Spread a layer of about 10 g. finely powdered silicon loosely in a 40 cm. long combustion tube which is placed over a row burner (Fig. 3, p. 2). Connect one end of the combustion tube with the chlorine generator, and draw out the other end to about the size of a lead pencil. Join this narrow end with a gas wash-bottle, using a rubber connector and pushing the ends of the glass tubes close together. Cool the wash bottle by surrounding it with a mixture of ice and salt, and arrange a glass tube to conduct the waste gases into the ventilating flue.

First of all, — and this is very important, — sweep the air completely out from the apparatus by passing a rapid stream of chlorine gas for about half an hour. After that, heat the combustion tube until the reaction begins and produces incandescence; the flames beneath the tube may be turned quite low while the reaction is progressing, and it is well to turn the tube from time to time on its long axis. All of the silicon is acted upon, and only a few flakes of silicon dioxide remain behind, while a trace of aluminium chloride condenses at the end of the tube.

Without using a thermometer, distil the impure product slowly from a fractionating flask with side-arm condenser (Fig. 7, p. 6). The greater part of the dissolved chlorine is thereby expelled, but to remove the last of it, let the distillate stand about a day in contact with mercury in a thick-walled bottle, stoppered with a cork (not a glass stopper), shaking vigorously from time to time until the liquid is decolorized. By again distilling, this time with a thermometer, the compound is obtained pure. Boiling-point, 58° to 60°. Yield, 35 to 40 g.

That portion of the distillate passing over above 60°, which, however, is small in amount by this method of preparation, contains a little silicon hexachloride, Si_2Cl_6, boiling-point 145° to 146°, and some silicon octachloride, Si_3Cl_8, boiling-point 210° to 215°.

Silicon tetrachloride is a colorless, mobile liquid, and shows a high refractive index for light. It fumes strongly in the air, and on being mixed with water it hydrolyzes, forming orthosilicic and hydrochloric acids:

$$SiCl_4 + 4\,H_2O = Si(OH)_4 + 4\,HCl.$$

Preserve the preparation in a sealed flask. Dependent preparation: Tetraethyl Silicate, No. 158.

Instead of starting with pure silicon, the directions of Gattermann[1] may be followed: Prepare an impure silicon by igniting 40 g. magnesium powder with 160 g. dried and sifted quartz sand, and chlorinate the resulting mixture of silicon and magnesium oxide by heating it to 300° to 310° in a long combustion tube, placed in a " bomb " furnace, while passing a current of dry chlorine. This method yields a product containing more of the hexachloride and octachloride than when, as by the first method, the chlorination is carried out at a higher temperature.

Silicon Chloroform. The compound $SiHCl_3$ can be obtained in a corresponding manner if, instead of chlorine, dry hydrogen chloride, free from air, is passed over the silicon powder at a temperature of 450° to 500°. For the preparation of this compound in larger quantities, and for its properties (boiling point, 33° to 34°), see Ruff and Albert, Ber. **38,** 2222 (1905).

52. Titanium Tetrachloride from Rutile.

A number of oxides which are not reduced by charcoal can be transformed into the corresponding chlorides by the simultaneous action of carbon and chlorine. This method was originated by Oersted in 1824, and perfected by Wöhler for a number of different oxides. It has been, for decades, the most important, if not the sole, method for the preparation of certain chlorides ($AlCl_3$, $SiCl_4$, $TiCl_4$, UCl_4 (No. 169), etc.). From a theoretical standpoint it is a good example of the displacement of an equilibrium by the removal of one or more of the products from the sphere of action, whereby a given reaction is enabled to become quantitative: the reduction of aluminium oxide cannot be accomplished by means of charcoal, but the oxides of carbon, on the other hand, can be reduced by aluminium; an equilibrium mixture of aluminium oxide, aluminium, carbon, and oxides of carbon, therefore, can contain only an infinitesimal amount of aluminium. If, however, this minute amount of aluminium in the mixture is removed continuously by causing it to combine with chlorine, an opportunity is thus afforded for a continuous reproduction of fresh quantities of aluminium from the reduction of its oxide, until the entire amount of the latter is exhausted.

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[1] L. Gattermann, Ber. **22,** 186; (1889) **27,** 1943 (1894).

The preparation of titanium tetrachloride from rutile is the most convenient laboratory method for obtaining pure titanium compounds from that inexpensive mineral. Instead of using carbon and chlorine separately, vapors of carbon tetrachloride may be conducted over the heated oxide; the same end may be attained by using sulphur chloride.

Mix 100 g. of finely powdered rutile intimately with 40 g. of lampblack, and knead the mixture, with the aid of as little starch paste as possible, into a thick, although still plastic mass. Shape the mass into pellets of about 0.5 cm. diameter, and dry them first in the hot closet, and then in a crucible placed in the charcoal furnace. Introduce the dry and very brittle pellets carefully into a wide combustion tube, and arrange the apparatus, which must be carefully dried, as shown in the sketch below (Fig. 16). Rubber connectors are to be avoided as much as possible. Before beginning the chlorination ignite the pellets again, this time in an atmosphere of carbon dioxide, in order to remove the last traces of moisture; and meanwhile start the evolution of chlorine in the generator. Then connect the apparatus for the first time with the receiver (capacity 200 to 300 c.c.), which is surrounded by ice. Conduct chlorine into the apparatus, and heat the tube, which rests in a combustion furnace, at first with small flames, then gradually bring it to a red heat. It

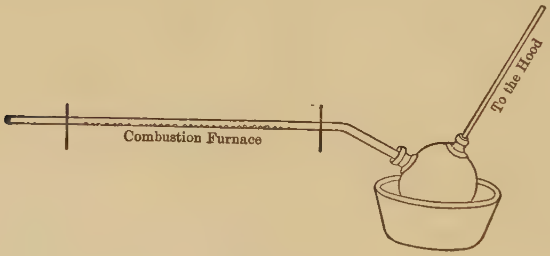

FIG. 16.

is essential to maintain a strong, steady stream of chlorine, the bubbles of which pass through the wash bottle so rapidly that it is just impossible to count them. Titanium tetrachloride collects in the receiver in the form of a liquid which is colored yellow by free chlorine and is clouded by small crystals of ferric chloride.[1] The operation requires about three hours. The amount of rutile prescribed is sufficient to yield enough material for two fillings of a combustion tube.

Filter the crude product through a dry Gooch crucible containing an asbestos-felt, and then allow it to remain in contact with mercury, or copper filings, in a thick-walled bottle closed with a cork stopper; occasionally shake it vigorously, adding a little fresh metal each time, until, at the end of about twelve hours, all the free chlorine has combined. A little sodium amalgam may be added toward the end of the process in order to remove traces of vanadium. After again filtering through a Gooch crucible, distil the clear liquid from a fractionating flask with a side-arm condenser (Fig. 7, p. 6). Boiling-point, 136° to 137°. The liquid has a strong refracting power for light, and it fumes in the air. Yield, 100 to 130 g. Dependent preparations: Titanium Disulphide, No. 58; Potassium Titanium Fluoride, No. 103.

Titanium Dioxide from Titanium Tetrachloride. Pour about 10 c.c. of titanium tetrachloride, a little at a time, into 200 c.c. of water, whereby hydrolysis takes place, although the hydrated titanium oxide which is formed remains in colloidal solution. Add a little sulphuric acid, and boil; titanic acid is thereby precipitated in a form which can be readily filtered. Wash the precipitate with water containing ammonium nitrate, dry it in the hot closet, and ignite it in a porcelain crucible until white titanium dioxide is left. In order to remove the last traces of sulphuric acid, which are retained very persistently, ignite the product several times with ammonium carbonate. Yield, almost theoretical.

Hydrogen Peroxide Reaction. Fuse a little titanium dioxide with potassium acid sulphate, and dissolve the melt in cold water. A few drops of this solution when treated with an aqueous solution of hydrogen peroxide show a brownish-yellow to yellow color.

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[1] If the rutile used has a high iron content, it can happen that the tube will become clogged with crystals of ferric chloride.

The reaction is extremely sensitive, and can be used as a test for hydrogen peroxide as well as for titanium. A drop of ordinary 3% hydrogen peroxide solution diluted with half a liter of water can be detected by adding a few cubic centimeters of the reagent. Molybdenum and vanadium compounds react similarly, though less strongly, with hydrogen peroxide.

53. Anhydrous Titanium Trichloride.

Titanium tetrachloride in aqueous solution may be reduced by metallic tin or zinc, or by electrolysis, to violet titanium trichloride; solutions of the latter have recently been recommended highly as reducing agents. The trichloride is obtained in an anhydrous condition by a method which is of quite general applicability. A mixture of titanium tetrachloride vapor and hydrogen is conducted through a red-hot tube whereby the trichloride deposits in the form of reddish-violet, non-volatile leaflets.

Place a tube made of difficultly fusible glass in a combustion furnace, and connect it, as shown in Fig. 17, on the one side with a 100 c.c. retort, and on the other side with a receiver of twice that size. Rest the receiver in a dish filled with ice, and add 40 to 50 g. of titanium tetrachloride to the retort.

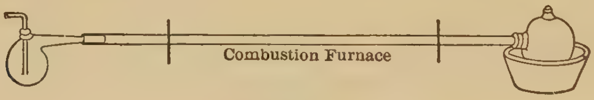

FIG. 17.

Fill the entire apparatus with hydrogen which is conducted through the inlet tube of the retort. As soon as the gas escaping at the other end is shown, on testing, to consist of pure hydrogen, heat the combustion tube to bright redness and heat the titanium tetrachloride nearly to the boiling-point by means of a small flame, meanwhile passing a rapid stream of hydrogen continuously through the apparatus. Regulate the temperature of the titanium tetrachloride so that, as nearly as possible, all of it is decomposed and none condenses unchanged in the receiver. If, however, this is not accomplished, pour back the distillate into the retort and repeat the process. Finally, disconnect the receiver (close the end of the tube with a cork carrying a short delivery tube bent downward) and heat the part of the tube projecting beyond the furnace by fanning it with a flame, until no more white vapors escape. Allow the apparatus to cool completely, and remove the preparation by the aid of a glass rod or a wire, after cutting the tube, if necessary, into several sections. The preparation should be protected from moisture, best by keeping it in a sealed tube. Yield, slight.

(c) *Sulphides.*

54. Phosphorus Pentasulphide;[1] Thermoelectric Determination of the Boiling-Point.

Mix 176 g. of flowers of sulphur with 62 g. of dry red phosphorus; if the phosphorus is moist, it should be washed with hot water, rinsed on a filter several times with water, then with alcohol, and dried in the hot closet.

Clamp a 750 c.c. round-bottomed flask to a ring-stand, under the hood, at a suitable height above a Bunsen burner. Introduce a spoonful of the above mixture into the flask, and after replacing approximately all of the air with carbon dioxide, heat until a reaction begins. Then remove the burner at once, and add spoonful after spoonful of the powder so that each portion immediately enters into reaction; toward the end heat the flask from time to time with the burner. Take care that neither the powder in the spoon nor the supply of unused material catches fire; keep a supply of sand on hand to throw on the blaze, and a pan to catch the liquid, in case the flask should break and its burning contents run out. Usually the preparation can be carried out without accident. After cooling, break the flask, and collect the gray and somewhat hygroscopic crude product.

Purify the substance by distilling it from a small, wide-necked, plain retort, rejecting the first few drops of distillate and collecting the main portion in a dry flask. To retain the heat, fold a piece of asbestos paper into a cone and place it over the neck and bulb of the retort. The distillate solidifies into a light-yellow, amorphous mass. Break the flask and transfer the product, after removing any fragments of glass, to a bottle which can be tightly stoppered. Yield, about 180 g.

A part of the preparation can be further purified by crystallization from carbon bisulphide. Place the material in a Soxhlet thimble, extract it for several days with carbon bisulphide in an automatic apparatus, and collect the crystals which have separated in the boiling-flask. The purified product melts at 275° to 276°, and 0.508 part dissolves in 100 parts of boiling carbon bisulphide.

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[1] Cf. A. Stock, Ber. **41,** 563 (1908).

Thermoelectric Determination of the Boiling-point. Le Chatelier's pyrometer is used for the measurement of temperatures up to 1600°. It consists of two wires, one of platinum and the other of 10% rhodium-platinum alloy, which, at one end, are fused together in the oxyhydrogen flame and at the other end are connected through a suitable measuring instrument.

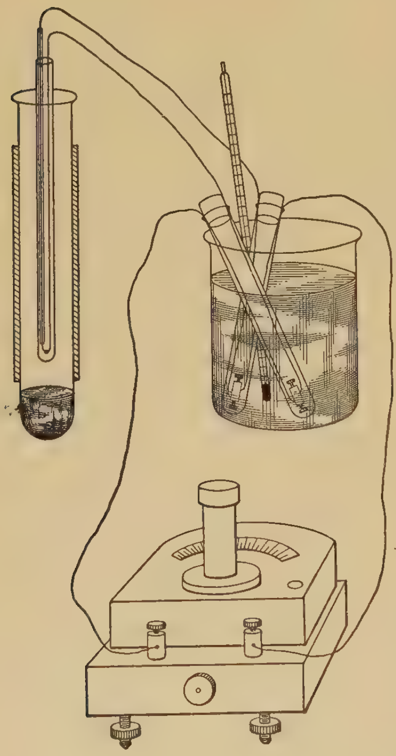

Fig. 18.

A difference between the temperature at the junction of the wires and that at the free ends gives rise to an electric current, the feeble potential of which may be measured by means of a sensitive voltmeter. In order to economize in the amount of platinum, the free ends of the pyrometer are connected to insulated copper wires leading to the measuring instrument. The two parts of the circuit where the connection with the copper wires is made are inserted in glass test-tubes, and the latter are closed by cork stoppers. The test-tubes are placed in a beaker filled with water to serve as a thermostat, and the beaker is enveloped in asbestos paper. In the voltmeter which is to be used for pyrometric work, a second scale is graduated to give directly the temperature readings, each division of the scale representing 10 degrees. In order to find the true temperature of the junction, the reading must be corrected by adding half the temperature of the thermostat. If the latter is maintained at 0°, by filling the beaker with ice, no correction is necessary. On account of the sensitiveness of the thermo-element toward chemical influences, the wires are protected by a long, narrow porcelain tube, to the closed end of which the thermoelectric junction is inserted. Inside this tube, one wire is isolated from the other by being placed inside a porcelain capillary (*a*, Fig. 19). The protective tube should, to save space, be made as narrow as possible, and it may be of glazed or unglazed porcelain; the latter will stand a higher heat, but is not impervious to gases; at temperatures up to red heat, a protective tube of Jena glass may be employed, which, particularly if the wires are insulated with mica, can be made of smaller bore. In setting up an apparatus for the pyrometric measurements of temperatures, special care should be taken to properly connect the thermo-element with the terminals of the voltmeter, to carefully isolate the pyrometer wires, and to see that the voltmeter is properly adjusted and set to the correct zero point.

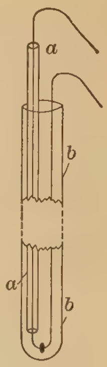

FIG. 19.

The pyrometer is best standardized by carrying out measurements with a few pure metals, the melting-points of which are accurately known.[1] Refer to the discussion, under Tin (No. 6, p. 15), of melting-point determinations.

To determine the boiling-point of the phosphorus pentasulphide, fasten a Jena-glass test-tube, about 40 cm. long and 4 cm. in diameter, in a perpendicular position, and place in it about 40 g. of the material. Around the middle part of the tube above the substance, wrap several layers of asbestos paper and secure the pyrometer so that the thermoelectric junction hangs two or three centimeters above the surface of the melted material. Heat the phosphorus pentasulphide to boiling with a large flame, meanwhile passing a slow stream of carbon dioxide into the upper part of the test-tube in order to prevent the ignition of the hot vapors when they come in contact with the air. The voltmeter rises slowly until it registers the temperature of the hot vapor, after which it remains constant. It is necessary, however, that the liquid should boil vigorously. The boiling-point determined in this way in the author's laboratory with the substance prepared as above, was 507° to 508° at 710 mm., which value agrees with that obtained by Bodenstein (508° at atmospheric pressure).

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[1] The National Testing Bureau at Berlin recommends the following fixed thermometry points. The values agree closely with those used by the Bureau of Standards at Washington, D. C.

B.P. of Oxygen, −183.0°
B.P. of Carbon Dioxide, −78.5
M.P. of Mercury, −38.89
M.P. of Ice, 0.00
Transf. P. of Sodium Sulphate, 32.38
B.P. of Water, 100.00
B.P. of Naphthalin, 217.96
M.P. of Tin, 231.84
B.P. of Benzophenone, 305.9
M.P. of Cadmium, 320.9
M.P. of Zinc, 419.4
B.P. of Sulphur, 444.55
M.P. of Antimony, 630
M.P. of Silver, 960.5
M.P. of Gold, 1063
M.P. of Copper, 1083
M.P. of Palladium, 1557
M.P. of Platinum, 1764

55. Black Mercuric Sulphide; Transformation into Cinnabar.

The black sulphide of mercury is always formed by the direct combination of the elements, as well as by the precipitation of a mercuric salt with hydrogen sulphide, but this modification changes slowly, of itself, into the more stable, red form (cinnabar). The transformation may be accelerated greatly by allowing the black sulphide to stand in a warm place in contact with a solution containing caustic alkali and alkaline sulphide; little by little the relatively more soluble black sulphide dissolves, and the more insoluble red form separates in a crystalline condition.

Triturate 50 g. mercury, 20 g. flowers of sulphur, and a little ammonium sulphide solution, in a large porcelain mortar. Mix the resulting black paste of mercuric sulphide, sulphur, and globules of mercury with 60 g. of a 20% caustic potash solution, and allow the mixture to stand at a temperature of about 50° (*e.g.*, on top of the hot closet). Replace the evaporated water daily, mixing up the mass each time with the pestle. When, at the end of a week at most, the mass has become of a pure red color, wash it by decantation with water, whereby the greater part of the excess of sulphur is removed, and then decant the cinnabar itself with water into an evaporating dish, allowing any lumps of the black sulphide to remain behind. Boil the material with a sodium sulphite solution to remove the remainder of the free sulphur, and wash the final product by decantation with boiling water. Drain the product on the suction-filter and dry it in the hot closet. Yield, 80 to 90% of the theoretical.

56. Sulphides of Tin.

Stannous Sulphide. Dissolve 12 g. of tin in 50 g. of concentrated hydrochloric acid, warming gently.[1] Dilute the filtered solution to 2000 c.c., and treat it, at the temperature of the water bath, with hydrogen sulphide until the precipitate settles clear. Collect the stannous sulphide upon a large plaited filter, wash it thoroughly with hot water, and allow it to dry over night on a porous plate. Break up the caked product which results and leave it in the drying closet, occasionally breaking up the lumps and grinding them to a powder, until the mass is entirely free from moisture.

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[1] The addition of 2.5 c.c. of nitric acid, of sp. gr. 1.2, together with the hydrochloric acid will cause the metal to dissolve very much more rapidly. The nitric acid is reduced to ammonium salt. (Translators.)

Stannic Sulphide. Triturate the stannous sulphide, prepared by the above directions, with half its weight of sulphur and 6 g. of ammonium chloride. Place the mixture in an Erlenmeyer flask, which should be about three-quarters filled, and bury the flask to its neck on a sand bath or place it on a Babo funnel, covering it with a cone of asbestos paper. Heat for two hours, not too strongly, but say sufficiently to keep the iron pan of the sand bath at a fairly bright red heat. Then, when the ammonium chloride and the excess of sulphur should be completely volatilized, allow the contents of the flask to cool. On breaking the flask, the stannic sulphide is obtained in the form of soft, glistening, yellow crystals. It is known in this modification by the name of *Mosaic Gold.* Impurities may be removed by decantation with water; they either float off or remain entirely behind.

Another method for preparing this compound is to start with stannic chloride and carry out the process as described for titanium disulphide, No. 58.

57. Green Manganese Sulphide.

Heat a solution of 40 g. crystallized manganous sulphate in 1200 c.c. of water to boiling in a 2-liter beaker. Blow in a vigorous current of steam, and add 300 c.c. of concentrated yellow ammonium sulphide, all at one time, while the solution is being agitated by the steam; the manganous sulphide formed appears reddish for the first moment, immediately turns yellowish, and soon becomes dark olive-green. Wash the precipitate, which settles well, by decantation with boiling water containing a little hydrogen sulphide; each volume of water added should be thoroughly mixed with the precipitate by blowing in steam. All of the ammonium salt is removed in the course of a few hours. A small amount of brown manganese oxide is formed during the process, by oxidation of the sulphide, but it floats on top of the liquid and is removed by the decantation.

Finally dry the manganous sulphide mud by draining it rapidly on a large suction filter, wash it with alcohol and dry it in a desiccator over sulphuric acid.

The preparation of green manganese sulphide does not always succeed the first time.

58. Titanium Disulphide.

1. *From Titanium Tetrachloride.*

This preparation furnishes an example of the decomposition of a chloride by hydrogen sulphide in the absence of water (cf. p. 68).

The apparatus described in No. 53 is used (Fig. 17, p. 84), but instead of hydrogen, hydrogen sulphide is employed. It is first passed through a small wash-bottle containing glycerol, in order that the bubbles may be counted, and through two U-tubes containing calcium chloride to dry the gas. In the retort 50 g. of titanium chloride are placed.

First of all pass a rapid stream of hydrogen sulphide through the apparatus and heat the combustion tube to dark redness; then heat the titanium chloride in the retort nearly to boiling, and keep it at that point by means of a small flame. The vapors of titanium tetrachloride charged with hydrogen sulphide are decomposed in the hot tube to TiS_2 and HCl; any unchanged titanium chloride that collects in the receiver is returned to the retort, again distilled, and the process repeated even a third time. The inlet tube for the hydrogen sulphide must not be too narrow, or it may become stopped with titanium disulphide formed within the retort. When all of the titanium tetrachloride has reacted, withdraw the retort, and, in order to remove all traces of tetrachloride from the product, pass a current of hydrogen or of carbon dioxide through the tube. After allowing the tube to cool, remove its contents in the manner described in No. 53. A product is obtained which consists of about 10 g. of dark brass-yellow leaflets similar to those of Mosaic gold.

Analyze one sample for titanium by roasting it in a porcelain crucible and weighing it as TiO_2; a second portion for sulphur by taking it up in aqua regia (or in the manner described below) and precipitating the highly diluted solution with barium chloride.

2. *From Titanium Dioxide.*

Titanium disulphide was first obtained by H. Rose (1823) on conducting vapors of carbon disulphide over glowing titanium dioxide. The theory of this method, which subsequently proved to be of importance for the preparation of sulphides, is the same as that of the preparation of chlorides from oxides and carbon tetrachloride (cf. Introduction to No. 52, p. 81).

Lead a fairly strong current of hydrogen sulphide through a wash bottle containing glycerol, a U-tube filled with calcium chloride, a wash bottle containing carbon disulphide, and into a piece of combustion tubing in which has been placed 4 to 5 grams of finely-powdered titanium dioxide (No. 52). Heat the contents of the tube to a bright red heat by means of a row burner with an asbestos hood (Fig. 3). The vaporization of the carbon disulphide may be hastened by placing the wash bottle in a beaker filled with lukewarm water. Do not heat the tube until the air has been completely expelled; during the heating revolve it a little on its axis from time to time in order that new portions of the dioxide may come to the surface. After about three hours the reaction is complete; allow the preparation to cool in the current of hydrogen sulphide.

The titanium sulphide has the appearance of a brown powder, but on being pressed it assumes a dark-yellow, metallic luster. In the analysis, titanium may be determined by roasting, and sulphur either by the method given above, or by heating the sample in a current of oxygen and collecting the gases evolved in ammoniacal hydrogen peroxide or in bromine water, eventually making this solution acid and precipitating it with barium chloride. The results show a somewhat too high titanium value, and too low sulphur, because, when prepared in this way, the sulphide invariably contains some titanium dioxide.

(*d*) *Nitrides.*

59. Hydrogen Cyanide, Mercuric Cyanide, Cyanogen, and Dithio-oxamide.

Carbon combines with nitrogen, absorbing heat, and forms the nitride, cyanogen:

$$2\ C + N_2 + 7100\ \text{cal.} = C_2N_2.$$

The endothermic nature of this substance (cf. p. 55) accounts for the formation of cyanogen compounds in the blast furnace, and for its presence in the sun, as shown by the spectroscope. When cyanogen is once formed, its rate of decomposition at a lower temperature is so small that it may be prepared pure in an indirect manner from its compounds and preserved undecomposed; cf. No. 64, Acetylene, and No. 67, Hydrogen Peroxide.

Free cyanogen gas which has the formula C_2N_2 should not be confused with the univalent radical CN. The radical CN forms a stable atomic grouping which behaves in the same manner as the halogen atoms in halides, and it bears the same relation to uncombined cyanogen as the chlorine ion, for example, bears to free chlorine.

For the preparation of cyanogen gas, hydrogen cyanide (hydrocyanic acid) is first prepared by Wöhler's method of treating either sodium or potassium ferrocyanide with sulphuric acid. The hydrogen cyanide, together with the residues, is worked over into mercuric cyanide and the latter decomposed by heat.

Hydrogen Cyanide from Potassium Ferrocyanide. Mercuric Cyanide.

$$2\,K_4[Fe(CN)_6] + 3\,H_2SO_4 = 3\,K_2SO_4 + K_2Fe[Fe(CN)_6] + 6\,HCN$$
$$6\,HCN + 3\,HgO = 3\,Hg(CN)_2 + 3\,H_2O.$$

Place a 400 to 500 c.c. flask on a Babo boiling funnel, and through the cork, which fits its neck tightly, pass a delivery tube leading to a condenser; fit the lower end of the condenser by means of another cork stopper into an adapter that just dips into 100 c.c. of water in the receiving flask. Introduce into the distilling flask 100 g. of coarsely broken potassium ferrocyanide and a cooled mixture of 70 g. concentrated sulphuric acid and 130 c.c. water. Distil until the residue in the flask consists of a thin white slime ["prussic acid residue," $K_2Fe[Fe(CN)_6]$(?)]. Set aside about 15 c.c. of the distillate. Dilute the remainder with water to a volume of 300 to 400 c.c. and add mercuric oxide (about 75 grams), shaking well, until the solution no longer smells of hydrocyanic acid (Caution) and shows a neutral or barely alkaline reaction. Then pour in the reserved 15 c.c. of hydrocyanic acid and evaporate the solution under a good hood till it crystallizes. If necessary, purify the preparation by recrystallization. Almost the theoretical yield of 85 to 90 grams is obtained.

In this and the following work regard should be paid to the extremely poisonous nature of hydrocyanic (prussic) acid, and the operations should be carried out under a well-ventilated hood in the special room for noxious materials, or in the open air.

Working up of the Prussic Acid Residues. Wash the residue remaining in the distilling flask by decantation with water, and then heat it upon the water bath with about 100 grams of 2-normal nitric acid, which oxidizes it to a mass resembling Prussian blue; the substance so formed contains potassium and is known as Williamson's Violet. Wash this pigment several times by decantation with water, suck it free from liquid on a hardened filter paper, and dry it in the hot closet. Yield, 40 grams.

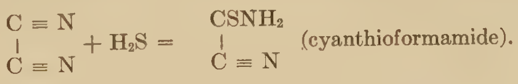
Mercuric cyanide can be prepared from Prussian blue or Williamson's violet by boiling the pigment with 2.25 times its own weight of mercuric oxide and forty times its weight of water. After the blue color has disappeared, filter the solution and boil the turbid filtrate with more of the Prussian blue until no more of it is decolorized and the solution reacts neutral. Add some animal charcoal, boil the solution again, filter, and finally evaporate to dryness. Recrystallize the residue from water.

Mercuric cyanide in aqueous solution is but slightly dissociated electrolytically, and on this account it fails to give a precipitate when treated with either silver nitrate or with sodium hydroxide. For the same reason mercuric oxide will dissolve in solutions containing potassium cyanide, forming mercuric cyanide and potassium hydroxide; the experiment should be tried.

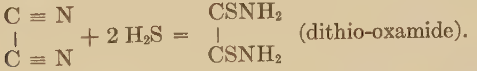
Cyanogen from Mercuric Cyanide. Heat about one gram of the mercuric cyanide strongly in a dry test-tube; cyanogen gas is evolved and burns with a yellowish-red flame, which is purple at the edges.

Dithio-oxamide.

Cyanogen unites with one or with two molecules of hydrogen sulphide:



$$\begin{array}{c} C \equiv N \\ | \\ C \equiv N \end{array} + H_2S = \begin{array}{c} CSNH_2 \\ | \\ C \equiv N \end{array} \quad \text{(cyanthioformamide).}$$



$$\begin{array}{c} C \equiv N \\ | \\ C \equiv N \end{array} + 2\,H_2S = \begin{array}{c} CSNH_2 \\ | \\ CSNH_2 \end{array} \quad \text{(dithio-oxamide).}$$

Dithio-oxamide is sometimes formed in qualitative analysis when hydrogen sulphide is passed into the solution containing potassium cyanide in the test for cadmium.

1. Saturate 100 g. of alcohol with hydrogen sulphide in a closed flask. Then conduct into the liquid some cyanogen gas, which is prepared by heating successively two portions of 10 g.

each of mercuric cyanide in a test tube fitted with a delivery tube. Finally, saturate the solution once more with hydrogen sulphide. After standing for some time a mass of small crystals is deposited; boil the mother liquor with bone-black and evaporate the filtrate in order to obtain another crop of crystals. Recrystallize the product from alcohol, or from a mixture of acetone and chloroform. Yield, 3.5 to 4 g.

2. Treat an aqueous solution of 25 g. copper vitriol with concentrated ammonia until the precipitate, which first forms, just disappears; decolorize the liquid by the addition of a barely sufficient amount of potassium cyanide solution (about 26 g. KCN) and then saturate with hydrogen sulphide. The solution first becomes yellow, then it appears red, and finally a red, crystalline powder separates. After standing for several hours in the ice-chest, separate the crystals from the liquor and recrystallize them from a little alcohol. The yield is small (about 0.5 g.) because in aqueous solution the greater part of the cyanogen is reduced to hydrocyanic acid. This is the reason for the use of alcohol in the first method.

60. Boron Nitride, BN.

Heat an intimate mixture of 5 g. finely powdered, anhydrous borax and 10 g. ammonium chloride, as hot as possible with the blast lamp in a covered platinum crucible surrounded by a clay mantle. After cooling, pulverize the porous contents of the crucible, and extract it several times with water containing a little hydrochloric acid. Boil the residue with pure water, collect it on a filter and dry it. Yield, about 0.3 g. The nitride prepared in this way always contains a little oxide.

Boron nitride is insoluble in water and in acids; on being boiled with caustic soda solution, it decomposes slowly, evolving ammonia; it is attacked more rapidly by fusion with sodium carbonate on platinum foil.

61. Magnesium Nitride, Mg_3N_2; Ammonia from the Atmosphere.

Fill a small iron crucible (3 cm. high and 5 cm. wide at the top) to two-thirds with 8 to 9 g. of magnesium powder, and make a tight joint with the cover by means of wet asbestos pulp. Likewise close with asbestos pulp a small hole which has been made in the cover. After drying, make a perforation in this last mass of asbestos by means of a fine needle. Dry the crucible, with its contents, in the hot closet.

Place the crucible in a hole made in a piece of heavy asbestos board, so that its greater part hangs below the asbestos, and direct the flame of a blast lamp sidewise against it. By this arrangement the flame gases are kept well away from the cover of the crucible. Turn the asbestos board with the crucible from time to time so that all sides are heated equally. Continue the heating for 30 minutes.

After cooling, remove the cover of the crucible and the upper layer of white magnesium oxide. Beneath the latter lies a light yellowish-green mass of nearly pure magnesium nitride, which is obtained to about 80% of the theoretical yield. If the heating is not continued long enough, dark places are found in the mass, caused by the presence of unchanged magnesium.

Magnesium nitride reacts violently with water with the formation of ammonia. To obtain the ammonia, place the whole contents of the crucible (without separating the oxide from the nitride) in a round-bottomed flask which is provided with a separatory funnel and with a right-angled tube leading to a condenser. Prolong the condenser with an adapter that just dips into 100 c.c. of water in a small flask. Cool the evolution flask by placing it in a dish of cold water, and then, at first slowly and later more rapidly, allow 75 c.c. of water to drop upon the nitride.[1] Finally, heat the contents of the flask with a small flame as long as ammonia continues to be evolved. Yield, 3 to 4 g. of ammonia, as determined by titrating an aliquot part of the distillate with 0.5 normal acid.

Calcium Nitride. Place a small shaving of metallic calcium on an inverted porcelain cover and set fire to it with a match. It burns with a light, yellowish-red flame, and both oxide and nitride are formed. Moisten the white combustion product with a few drops of water, and test with Nessler's reagent for ammonia.

The chemical reaction is the same for both the magnesium and calcium nitrides. A part of the metal serves to free the air of oxygen, while the remainder combines with the nitrogen that is left. By the hydrolysis of the nitride, ammonia and the hydroxide of the metal are formed. The possibility of obtaining ammonia from the nitrogen of the air, with the intermediate formation of a nitride, was first pointed out by Wöhler in 1850 when his method of preparing boron nitride was published.

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[1] Since the reaction produces intense heat, it is well, in order to avoid breaking the flask, to place in the bottom of the flask a layer of sand and on top of this the nitride mixed with sand.

62. Chromium Nitride, CrN.

Heat 5 to 10 g. of violet, anhydrous chromium chloride (No. 44) in a 25 to 50 cm. tube of difficultly fusible glass, at first gently and then strongly with a row burner (Fig. 3, p. 2). Meanwhile pass through the tube a current of ammonia gas, which is obtained by heating a concentrated solution of ammonia and drying the gas successively in a lime-tower and a U-tube containing lime. Leave the reaction tube entirely open at one end, since if an ordinary delivery tube is used to carry away the waste gases, it soon becomes stopped with sublimed ammonium chloride. Carry out the experiment under the hood and continue the heating until no more vapors of ammonium chloride escape. After cooling, pulverize the reaction product and once more ignite it in an atmosphere of ammonia. Yield, nearly theoretical.

Chromium nitride is very stable towards warm caustic soda solution, and hot concentrated sulphuric acid reacts with it but slowly. To test its purity, boil a small sample with chloride-free caustic soda and test the solution obtained for chloride. If it is desired to remove traces of chromium chloride from the preparation, it may be treated in the cold with dilute hydrochloric acid and a little tinfoil, then washed with water, drained, and dried at 110° to 120°.

Chromium nitride, on being heated upon a porcelain crucible cover over the blast lamp, changes to dull, grayish-green chromic oxide.

(*e*) *Phosphides.*

63. Magnesium Phosphide, Mg_3P_2.

Draw out one end of a 35 cm. long combustion tube so that its diameter is 0.6 to 0.9 cm., and connect this end by a piece of rubber tubing with two drying bottles and a Kipp hydrogen generator. Insert two porcelain boats into the tube, the one nearest to the source of hydrogen containing about five grams of red phosphorus and the other four grams of magnesium powder. The phosphorus must be perfectly dry (cf. p. 85). Erect the apparatus under the hood.

After filling the apparatus with hydrogen (Test!), heat the tube slightly through its entire length to expel moisture; then, while maintaining a steady current of hydrogen, heat both boats as equally as possible by means of two Bunsen burners so that phosphorus vapor is carried over the magnesium and a violent reaction takes place. When all the phosphorus has volatilized, allow the contents of the tube to cool in the atmosphere of hydrogen.

Magnesium phosphide when thrown into water is decomposed, and phosphine is set free. This gas has a very offensive odor; it is combustible, but it does not, like the impure phosphine that is commonly prepared, take fire spontaneously.

(*f*) *Carbides.*

64. Calcium Carbide; Acetylene from Calcium Carbide; Benzene from Acetylene.

Calcium Carbide. Heat 0.5 g. of lampblack strongly in a porcelain crucible for a few minutes; after it has cooled mix with it 0.5 g. of thin shavings of metallic calcium, and heat the mixture strongly with the blast lamp for a few minutes. After cooling there is found in addition to lampblack a sintered white mass which contains some calcium carbide; on testing it with water, acetylene is formed.

Acetylene from Calcium Carbide. Allow water to drop slowly from a dropping funnel upon a few pieces of commercial calcium carbide in a half-liter flask. Pass the acetylene evolved through a solution of sodium plumbite in order to remove any hydrogen sulphide, and through an acid solution of copper sulphate to take out any phosphine. Acetylene burns with a brilliantly luminous and, unless in a special burner, very smoky flame. Before igniting the gas it should be tested to see whether all the air has been removed from the apparatus.

At the temperature of the electric arc, acetylene can be formed from its elements with absorption of heat. At a bright red heat it decomposes, but at lower temperatures, although it is likewise unstable, its rate of decomposition is extremely slow. (Compare with the similar relations which exist for cyanogen, No. 59, and hydrogen peroxide, No. 67.)

At a dull red heat acetylene polymerizes to a considerable extent, forming benzene: $3\,C_2H_2 = C_6H_6$. The presence of benzene in coal-tar may be attributed to this reaction; indeed, this supposition is supported by the fact that the yield of benzene in the tar sinks if the temperature of the gas retorts is raised.

Benzene from Acetylene. Prepare pure acetylene, as directed above, and pass a *strong* current of it for two hours through a glass tube that is heated to dull redness in a combustion furnace (the air must be expelled by acetylene before the tube is heated!). Lead the products, escaping from the combustion tube, through a condenser; in this way a few cubic centimeters of an oil having the odor of coal-tar are obtained. By distilling this product, a crude, colorless benzene is obtained which boils between 70° and 90°. For the further identification of this substance as benzene it may be converted into nitrobenzene, aniline, and then mauvein. Refer to a text-book on organic preparations, for example Gattermann, "Laboratory Methods of Organic Chemistry" (Translated by W. S. Shober).

CHAPTER IV.

COMPOUNDS CONTAINING A COMPLEX NEGATIVE COMPONENT.

THE modern conception of complex compounds arose from the necessity of classifying the compounds formed by the union of two simple salts. Those composite salts which in aqueous solution are dissociated entirely into the simple salts, or their ions, are classed as double salts; those which, instead of dissociating into the simple salts, give characteristic ions of their own — for example, simple metal cations and composite metal-containing anions — are classed as complex salts:

$$KMgCl_3 = KCl + MgCl_2 = K^+ + Mg^{++} + 3\,Cl^- \text{ (double salt)},$$
$$K_2[HgI_4] = 2\,K^+ + [HgI_4]^{--} \text{ (complex salt)}.$$

In such a complex compound, the composite part which remains intact during dissociation is known as a *complex radical* or *complex ion* [1] and may be regarded as the negative component of a new acid; sometimes indeed the complex acid can be prepared in a free state, for example, hydroferrocyanic acid (No. 108). The individual constituents of a complex ion, since they are not present in the free state, do not show all the reactions which are characteristic of the simple ions; it is this reduced ability of metals contained in complex radicals to react, which forms the most important criterion of this class of compounds.

The conception of complex compounds has, however, extended considerably beyond the range of these composite salts. In the first place, the distinction between double and complex salts is merely a qualitative one. Transition forms are known in which the simple salts and their ions as well as the complex ions are found among the dissociation products; the nature and extent of the dissociation is also dependent to a marked degree upon the nature of the solvent and upon the concentration. Again, no essential distinction can be drawn between the compounds with complex, metal-containing anions and those which are formed by the addition of NH_3, H_2O, NO_2, etc., to the metal ion of a simple salt, and in which the metal-containing cation is complex and the activity of its constituents is restricted. Finally, certain binary substances, such as for example the oxides, which themselves possess none of the characteristics of salts, can produce salts (or acids or bases) by uniting with one another. Thus the ordinary oxygen-acids are formed by the union of water and acid anhydride, and the salts of the oxygen-acids by the union of metal oxide and non-metal oxide. Here also there are produced, quite in accord with the interpretation of complex salts, new ions, the separate constituents of which are incapable of entering into independent chemical reactions:

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[1] It is a quite common practice to indicate complex ions in chemical formulas by enclosing them in brackets.

$$H_2O + SO_3 = H_2[SO_4],$$
$$H_2[SO_4] = 2\,H^{+} + [SO_4]^{--}.$$

Thus the sulphate radical does not show the reactions of sulphur any more than the ferrocyanide radical exhibits those of iron.

Since manifestly every compound containing more than two elements can under certain conditions behave in such a manner as to indicate the grouping of two of its constituents into a complex, it appears more rational *to include under complex compounds all substances which are produced from simple compounds by the addition of one or several elements;* in most cases the complex radical behaves, like the hydroxyl group, as a unit, and can thus be treated as a substituent of an atom.

The most essential difference between the complex and the simple compounds lies in the great variety of ways in which the former can react or dissociate, and this is more evident in proportion to the number of constituents. There is but one way in which electrolytic and non-electrolytic dissociation can take place in simple compounds. With complex compounds, on the other hand, the point of division is usually not the same by the electrolytic as by the non-electrolytic dissociation:

$CaCO_3 = Ca^{++} + CO_3^{--}$ (electrolytic dissociation).[1]
$CaCO_3 = CaO + CO_2$ (non-electrolytic dissociation).[1]

Non-electrolytic dissociation may be of very different types:

$KClO_3 = KCl + 3\,O$ (Nos. 74 and 75).
$NaNO_3 = NaNO_2 + O$ (No. 79).
$Na_2S_2O_3 = Na_2SO_3 + S$ (No. 90).
$KPbI_3 = KI + PbI_2$ (No. 105).
$NH_4Cl = NH_3 + HCl$ (No. 120).
$Ni(NH_3)_6Br_2 = NiBr_2 + 6\,NH_3$ (No. 128).

Classification of Complex Compounds. Of the various ways in which complex compounds can dissociate, the electrolytic dissociation exceeds all others as regards frequency of occurrence. We may classify the complex compounds, therefore, as: 1. Those with a complex radical which yields an ion of negative charge (Chapter IV); 2. Those with a complex radical which yields an ion of positive charge (Chapter V); 3. Those characterized by very little or no capacity for electrolytic dissociation (Chapter VI).

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[1] According to whether the one or the other possibility of dissociation is to be brought especially to notice, two methods of writing the name and symbol have been devised: $CO_2 \cdot CaO$, " carbonate of lime "; $CaCO_3$, " calcium carbonate "; but it would be just as biased to defend the older name as being the only satisfactory one as it would be to reject it as " unscientific."

Within the class of compounds possessing complex anions that sub-class will first be treated which comprises the compounds containing *homogeneous complexes.* Homogeneous complex anions arise, as the name implies, when one or more additional atoms of the same element are joined to the negative constituent of a binary compound,

$$K_2S + 3\,S = K_2S_4.$$

Homogeneous complex compounds can be distinguished from simple compounds of the general formula $A_m\,B_n$ by the fact that the greater number of negative atoms is not due to an increased valence of the positive component, but rather to an increased combining power of the negative part originally present in the mother-substance. $FeCl_2$ differs from $FeCl_3$ in the valence of the iron. Aqueous solutions of $FeCl_2$ and $FeCl_3$ are identical with regard to their anions but different with regard to the cations; in aqueous solutions of KI and KI_3, however, the exact opposite is true.

Only a few compounds with homogeneous complex cations are known.

The part played by the valence theory in the interpretation of complex compounds is varied. In some cases, as with sulphuric acid, it offers certain advantages in its original form. In other cases an enlargement of our valence ideas seems necessary (see Complex Halogen Salts, p. 140).

COMPOUNDS WITH HOMOGENEOUS COMPLEXES.

(*a*) *Peroxides.*

65. Sodium Peroxide.

Arrange a train of apparatus so that air may be drawn by means of a suction pump through one wash-bottle containing sodium hydroxide and two more containing concentrated sulphuric acid, and then into a wide, 30 cm. long, combustion tube which is to be heated on a row burner with an asbestos cover (Fig. 3). The other end of the combustion tube is made narrower and fitted to an air filter which serves to hold back sodium peroxide dust. This filter consists of a 30 cm. long and 3 cm. wide glass tube loosely filled with asbestos fibers. Between the air filter and the pump, place an empty suction flask to serve as a safety bottle. Into the combustion tube introduce an aluminium boat, about 16 cm long and as deep as possible, which can be prepared from thin aluminium foil; in the boat place 2 to 3 g. of sodium. Since, during the progress of the experiment, the sodium will tend to flow in a direction opposite to that of the air current, the combustion tube together with the burner should be placed in a slanting position so that the end at which the air enters is uppermost.

Heat the sodium to above its melting-point and draw air over it; at about 300°, it takes fire. Then lower the flame, for from that point on the combustion proceeds almost without any application of external heat. Continue to pass a vigorous current of air until the reaction has ceased. The yield is 4 to 5 g. of bright yellow sodium peroxide, which must be protected from moisture.

66. Barium Peroxide.

At a dull red heat, dry barium oxide is changed by the oxygen of the air to barium peroxide. In carrying out the reaction, the air must be free from moisture and from carbon dioxide. Since the barium peroxide gives off its oxygen again at the same temperature and a reduced oxygen pressure, or at the same pressure and a higher temperature, a technical process for obtaining pure oxygen from the air according to the reversible reaction

$$BaO + O \rightleftarrows BaO_2$$

has been developed. Barium oxide cannot be prepared conveniently from barium carbonate, at least not on a small scale, because the decomposition temperature of the latter lies too high.

Crude Barium Peroxide. Place 130 g. of barium nitrate in a large clay crucible and heat it in a charcoal furnace with slowly rising temperature, to a dull red heat. After cooling break the hard, porous, gray contents of the crucible into small lumps and transfer it, before it can attract moisture, into a weighed combustion tube. Determine the quantity of barium oxide by weighing the tube and contents. Heat the tube in a combustion furnace to a barely perceptible redness, and then draw through it a current of air which has passed through caustic soda solution and then through concentrated sulphuric acid. After two or three hours, let the tube cool and determine the gain in weight, which should be one-tenth the original weight of the barium oxide; if it is less, the preparation must be heated again in the current of air.

Pure Barium Peroxide. Dissolve the barium peroxide, a little at a time, in the calculated amount of ice-cold 1% hydrochloric acid and add barium hydroxide solution to the cloudy liquid until a precipitate consisting chiefly of metal hydroxides, which are present as impurities, just forms. Filter, and precipitate the filtrate completely with barium hydroxide, whereby a fine, crystalline powder of barium-peroxide-hydrate, $BaO_2 \cdot 8\ H_2O$, is formed. Drain the precipitate and dry it in the steam closet.

67. Hydrogen Peroxide.

The oxidation of water to hydrogen peroxide takes place with absorption of heat:

$$2\,H_2O\text{ (liquid)} + O_2 + 44{,}320\text{ cal.} = 2\,H_2O_2\text{ (liquid)}.$$

Hydrogen peroxide is thus endothermic as regards its formation from water and oxygen. In accordance with the relation which exists between the equilibrium constants of the mass-action law and the temperature (cf. p. 47), it follows that the quantity of hydrogen peroxide in an equilibrium mixture must increase with rise of temperature, and that therefore in order to obtain hydrogen peroxide synthetically by the above reaction it is necessary to work at as high a temperature as possible. Even at 2000° there is but little peroxide present in the equilibrium mixture.[1] At low temperatures hydrogen peroxide is not stable at any appreciable concentration; in fact a liquid containing a high percentage of it is explosive. The velocity at which hydrogen peroxide decomposes, when in the region of instability as regards temperature or concentration, increases (as does the velocity of all reactions) with rise of temperature.[2] If then it is desired to obtain the hydrogen peroxide produced by a reaction at a high temperature, it is necessary to cool the reaction products very rapidly to a point where the decomposition velocity is inappreciable. When thus chilled the hydrogen peroxide continues to exist, as it were, in a supercooled condition. This end is accomplished, for example, when an oxyhydrogen flame comes in direct contact with a piece of ice and thereby an extremely sudden drop in temperature is brought about. Cf. Cyanogen, No. 59, and Acetylene, No. 64.

The principle of preserving the equilibrium concentrations, as they exist at high temperatures, by means of sudden cooling was first introduced by Deville in 1863 and applied in the construction of his "hot and cold tubes." A narrow silver tube cooled by running water was placed in the center of a white-hot porcelain tube at the walls of which the gas-reaction to be measured reached its high-temperature equilibrium; the reaction-products on coming in contact with the inner tube were chilled, and thus prevented, partially at least, from undergoing the reverse reaction. In recent years many equilibria, in which concentrations of measurable magnitude are reached only at high temperatures, have been studied in this manner. The mixtures are cooled, without suffering change in concentration, to temperatures at which analytical measurements are possible. The quantitative preservation of the concentration fails, however, in the case of hydrogen peroxide on account of its great decomposition-velocity.

The velocity of many reactions can be increased by means of catalyzers, as well as by rise of temperature. The decomposition of hydrogen peroxide, since it takes place with conveniently measurable rapidity at ordinary temperatures, offers an excellent opportunity for studying the effect of various catalyzers. In this way a remarkable analogy between organic ferments and inorganic catalyzers has been discovered. Cf. No. 20. Hot solutions of hydrogen peroxide are decomposed rapidly at the rough places on porcelain or glass apparatus.

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[1] At 2000° according to Nernst (1903) less than 1% H_2O_2 exists in a mixture of water vapor and oxygen, each at 0.1 atmosphere pressure.

[2] In order to keep the temperature low during the distillation of hydrogen peroxide, it is customary to work in a vacuum.

A. *Hydrogen Peroxide from the Oxy-hydrogen Flame.* Let a hydrogen flame one-half centimeter long, burning from a glass tip, play against a piece of ice in a watch glass, until all the ice is melted. The presence of hydrogen peroxide in the resulting liquid may be easily shown by means of a titanium solution (see p. 83).

B. *Hydrogen Peroxide from Barium Peroxide.* Add, little by little, some pulverized, crude barium peroxide[1] (No. 66) to a mixture of 0.6 of its weight of concentrated sulphuric acid and 300 c.c. of water; the liquid must be kept cold by ice both inside and outside the vessel. Neutralize the excess of acid with barium carbonate, let the precipitate settle, filter, and distil the solution on the water bath.

For the distillation use a liter round-bottomed flask with a stopper through which pass two glass tubes; one is quite narrow and terminates below in a long, fine capillary and above in a rubber tube with a screw-cock. The other tube leads from the flask to a long condenser; the lower end of the latter is fitted to a suction bottle which serves as a receiver. All parts of the apparatus must be closed with tightly-fitting stoppers. Evacuate the apparatus, but allow a fine stream of air bubbles to flow continuously from the capillary through the liquid in the flask, in order to avoid bumping; the rate of flow of this air current is to be regulated by the screw-cock. Distil over about one-third of the contents of the flask and test the distillate for hydrogen peroxide as described below; it should be practically pure water. Then empty the receiving bottle and distil as before until all of the remaining liquid has passed over.

Qualitative Tests for Hydrogen Peroxide.

1. *Titanium Sulphate Test* (cf. p. 83).

2. *Chromic Acid Test:* To a few c.c. of a chromate solution weakly acidified with sulphuric acid, add a few drops of hydrogen

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[1] The use of barium peroxide hydrate has also been recommended.

peroxide, and then shake with about 1 c.c. of ether; an intensely blue compound of chromium is formed which is more soluble in ether than in water and passes, therefore, into the ether layer.

3. *A very dilute solution of potassium iodide* on being treated with a small amount of hydrogen peroxide slowly turns yellow (or blue if starch is also added) as a result of the separation of iodine. This reaction is catalytically accelerated, somewhat by acetic acid, more by mineral acids, and most of all by ferrous sulphate.

Quantitative Determination of Hydrogen Peroxide. Dilute 10 c.c. of the preparation to about 300 c.c., acidify strongly with sulphuric acid, and titrate with potassium permanganate: $2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$. 1 c.c. of 0.1-normal $KMnO_4$ solution = 0.0017 g. H_2O_2.

C. *Hydrogen Peroxide as a By-product in Slow Atmospheric Oxidations.*

Schoenbein, in 1864, established the fact that hydrogen peroxide is produced when metals, or their amalgams, are shaken with water containing dissolved oxygen:

$$Zn + 2\,H_2O + O_2 = Zn(OH)_2 + H_2O_2.$$

It was shown by M. Traube,[1] in 1893, that the formation of hydrogen peroxide according to the equation becomes quantitative if the reaction is allowed to take place in the presence of calcium hydroxide, for then the peroxide is precipitated as the difficultly soluble calcium peroxide and is thus withdrawn from the sphere of action.

Such an oxidation in which twice as much oxygen is used as is necessary for the primary process itself, the other half of the oxygen being used in some secondary reaction — mostly in the formation of hydrogen peroxide — is of frequent occurrence both in organic and inorganic chemistry and is known as "auto-oxidation." Inasmuch as both the primary and secondary reactions require the same quantity of oxygen and since they do not take place independently of one another, — hydrogen peroxide is not formed at ordinary temperatures from water and oxygen (see above), — it is necessary to assume the existence of some peculiar form of reaction-mechanism. Views regarding this, however, differ widely; for example, the hydrogen peroxide may be regarded as a decomposition product of some higher oxide, such as zinc peroxide, which is formed in the primary reaction; or it may be assumed with Traube that a dissociation of the water molecules takes place, the hydroxyl groups combining with the metal and the hydrogen atoms combining with undissociated oxygen molecules.

Place 200 c.c. of water, 6 g. of slacked lime, 2.5 g. of potassium hydroxide, and 30 g. of mercury in a thick-walled liter flask. Amalgamate the surface of about 0.5 g. of zinc turnings by treating with a solution of mercuric chloride, and then add the zinc a little at a time to the contents of the flask. On shaking vigorously, the zinc dissolves completely in the mercury and then becomes oxidized according to the equation given above. To show the presence of hydrogen peroxide, treat samples of the resulting turbid liquid with an acidified iodide-starch solution containing a drop of ferrous sulphate, or with a titanium sulphate solution.

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[1] Ber. **26**, 1471 (1893).

(*b*) *Polysulphides.*

68. Ammonium Pentasulphide, $(NH_4)_2S_5$.

The sulphur which is bound directly to the metal in metallic sulphides is capable of taking on more sulphur to form polysulphides (Berzelius). The additional binding power of the sulphur seems to be influenced to a high degree by the metal with which it is combined. Polysulphides of the alkali metals are numerous and well known, as are also many of the alkaline earth group; but for the heavy metals either none exist or they play, at most, a subordinate rôle. Polysulphides of the alkali metals can be obtained by fusion (sulphur livers), those of cæsium and rubidium with the general formula M_2S_n, in which $n = 2, 3, 4, 5$, and 6, having been identified;[1] polysulphides can also be formed by dissolving sulphur in solutions of the monosulphides and thereupon crystallizing or precipitating the product. (See below.) Of the polysulphide solutions, those of the tetrasulphides with the ion S_4^{--} are especially stable.[2] Besides the types already mentioned, other polysulphides have been obtained under varying conditions from such solutions, but the individuality of some of them is doubtful.

Saturate 25 c.c. of concentrated ammonia solution with hydrogen sulphide in a closed flask, add another 25 c.c. of the ammonia, and then dissolve in this mixture as much roll sulphur as possible (about 25 g.) at 30° to 40°. Filter off the excess of sulphur and to the yellow solution in an Erlenmeyer flask add an equal volume of 95% alcohol. After the solution has stood over night in the ice-chest, an abundant crystallization of intensely yellow needles of ammonium pentasulphide is obtained. Drain the crystals, wash them with alcohol and ether and allow them to dry for a day in a vacuum desiccator over quicklime upon which a few drops of concentrated ammonia have been poured. The yield is about 40 g. On long standing, the crystals become lighter colored, due to decomposition. Determinations of ammonia and sulphur confirm the above formula.

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[1] W. Biltz and Wilke-Doerfurt, Ber. **38**, 123 (1905); Z. anorg. Chem. **48**, 297; **50**, 67 (1906); J. S. Thomas and A. Rule, Chem. Soc. **111**, 1063 (1917).

[2] Küster, Z. anorg. Chem. **43**, 53 (1904); **44**, 431 (1905).

(*c*) *Polyhalides.*

Polysulphides and polyhalides are very closely related. The latter likewise occur chiefly as salts of the alkali and alkaline earth metals and as the free halogen acids. The stability of the compounds increases very rapidly in the series of the alkali metals with the increase in the atomic weight of the metal. From cæsium and rubidium a large number of both simple and mixed polyhalides of the type MHa_3 and MHa_5 ($Ha = Cl, Br$, or I) have been obtained. As regards the stability of its polyhalogen compounds, ammonium comes next to the higher alkali metals; still more stable are the substituted ammonium salts, namely, the polyhalides of the complicated alkaloids, such as coniin, nicotin, atropin, narkotin, and of the diazonium salts.

69. Ammonium Tribromide, $NH_4[Br_3]$.

Add 8 g. of bromine[1] to a lukewarm solution of 10 g. ammonium bromide[2] in 12 g. of water, whereupon the temperature of the mixture rises a little. Allow the solution to stand over sulphuric acid in a vacuum desiccator which, if possible, should be placed in an ice-chest. Prismatic crystals, or lamellar aggregates, of the color of potassium pyrochromate separate from the solution which still contains free bromine. After one or two days drain the crystals and dry them in a vacuum desiccator containing a small dish of bromine in addition to sulphuric acid (the preparation would lose bromine to an atmosphere free from that element). The yield is about 10 g. Analyze the product as

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[1] This is only half the calculated amount. The use of more bromine does not improve the yield.

[2] Ammonium bromide may be prepared either by the neutralization of hydrobromic acid (No. 35) with ammonia or by the action of bromine on ammonia. According to the latter method, allow 13 g. bromine to flow drop by drop from a dropping-funnel into 130 c.c. of 2-normal ammonia in a flask, which is surrounded by ice and is constantly shaken.

$$8\,NH_3 + 3\,Br_2 = 6\,NH_4Br + N_2.$$

Evaporate the solution on the water bath, and if desired powder the residue and dry it in the steam closet. The salt may be purified by recrystallization. Dissolve it in its own weight of boiling water, cool the solution with ice, and add an equal volume of alcohol; recover the rest of the salt from the mother-liquor by evaporating and crystallizing in a similar manner.

follows: First dissolve a sample of about 0.25 g. in a solution of potassium iodide and titrate with 0.1-normal thiosulphate; second, expose about 0.25 g. to the air in a moderately warm place until it has become colorless, and weigh the residue of ammonium bromide which is left.

On dissolving the tribromide in water, free bromine separates in considerable quantity and one molecule of Br_2 can be completely removed by shaking the solution with carbon bisulphide, or chloroform.

70. Law of Distribution; Proof of the Existence of Potassium Tribromide and Potassium Tri-iodide.

A. *Law of Distribution.*

If to two non-miscible solvents standing in contact with one another, a third substance is added which is soluble in both, the ratio of the concentration[1] of this substance in the two solvents after equilibrium has been established, i.e., the distribution coefficient, will be constant for a given temperature provided the solute has the same molecular weight in both solutions:

$$\frac{c_1}{c_2} = k.$$

If the dissolved substance exists in one of the two solvents in a dissociated or associated condition, the distribution law holds only for the same sort of molecular aggregate in both solvents. This fact finds expression in the formula in such a way that now the ratio $\frac{c_1^{n_2}}{c_2^{n_1}}$ remains constant if n_1 and n_2 are the number of simple molecules associating to give the prevalent form of molecules in the respective solutions.

I. Dissolve about 4 g. of succinic acid in 200 c.c. of water, shake the solution with 50 c.c. of ether in a 500 c.c. separatory funnel, allow the two liquids to separate, and titrate 10 c.c. from both layers with 0.1-normal sodium hydroxide, using phenolphthalein as an indicator. To what is left in the separatory funnel add about 100 c.c. of water and some ether, shake thoroughly again, and titrate portions of 20 c.c. each from both layers. Again add 50 c.c. of water and half as much ether, and determine the concentrations in 20 c.c. portions. Finally add 100 c.c. of water and this time titrate 40 c.c. portions. The four distribution coefficients calculated from the data obtained should be practically equal. Succinic acid is about six times as soluble in water as in ether.

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[1] Concentration = the amount of substance contained in a unit of volume, i.e., $\frac{m}{v}$.

II. Dissolve 10 g. of benzoic acid in a mixture of 100 g. of water and 100 g. of benzene; shake a little longer after it is all dissolved until the distribution equilibrium is reached, and titrate 10 c.c. from each layer. Add 50 c.c. of water and again shake vigorously, repeating this several times in succession and titrating both layers after each addition. Nearly constant values are obtained in this experiment if the square of the solubility in water is divided each time by the solubility in benzene; the molecular weight of benzoic acid dissolved in benzene is nearly twice as large as in water.

B. *Proof of the Existence of Potassium Tribromide in Aqueous Solution.*

Bromine dissolves more freely in a potassium bromide solution than in water, this being due to the formation of the potassium salt of the complex brom-hydrobromic acid, $K[BrBr_x]$. The salt has never been obtained in a solid form suitable for analysis; but its composition can be derived, with the aid of the mass-action law and the law of distribution, by finding which of the assumptions, $x = 2$, $x = 4$, etc., leads to conclusions agreeing with the facts found experimentally. Calculating first on the basis of the complex ion Br_3^- (i.e., $x = 2$), this ion would be partially broken down in solution into simple bromine ions and free bromine:

$$Br_3^- \rightleftarrows Br^- + Br_2.$$

For the state of equilibrium, the mass-action law gives:

$$\frac{[Br^-]\,[Br_2]}{[Br_3^-]} = k.$$

The three concentrations which are in equilibrium according to the above equation may be determined by preparing a concentrated solution of bromine in carbon bisulphide and shaking one portion of it with water, and a second portion with a potassium bromide solution of known molecular concentration,[1] A. In each experiment the molecular quantities of bromine, D and B, which pass into the aqueous layer are determined; the excess of bromine in the second case is equal to that combined in the complex: thus, $[Br_3^-] = B - D$.

Furthermore, $[Br_2] = D$; according to the distribution law, the amount of free bromine existing in the potassium bromide solution, as well as that existing in the pure water, is determined solely by the concentration of bromine in the carbon bisulphide layer.

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[1] The molecular concentration is the amount of substance dissolved in one liter divided by its molecular weight.

Finally, $[Br^-] = A - (B - D)$, i.e., the equilibrium concentration of bromine ions is equal to the difference between the original concentration of the bromine ions and that of the part which forms the complex. By inserting these values in the mass-action equation, we obtain:

$$\frac{D[A - (B - D)]}{B - D} = K.$$

Mix one volume of bromine with four volumes of carbon bisulphide and add 5 c.c. of the mixture to each of six 50 c.c. glass-stoppered bottles; add about 20 c.c. of water to each of two of the bottles, and to the other four add equal volumes of potassium bromide solution of the following normal concentrations:

$$A = 1/1; \quad 1/2; \quad 1/4; \quad 1/8.$$

Establish equilibrium between the layers by shaking vigorously for a long time; place the bottles in water at room temperature, and give them an occasional lateral motion in order to make the drops of carbon bisulphide solution floating on the surface sink. After about an hour, when the aqueous layer has become *entirely* clear, pipette off 10 c.c. from each bottle, and after adding potassium iodide, titrate with 0.1-normal thiosulphate to disappearance of color. In this way the concentrations B and D are obtained. Substitute these values, as well as the corresponding values of A, in the mass-law equation and see whether K remains constant throughout the experiment. If this is the case, it proves the existence of the compound KBr_3. It is a good plan to make the assumption, by way of a check, that more than one molecule of bromine combines with the potassium bromide in the formation of the complex, to substitute the values in the corresponding mass-law equation, and to compare the values of K thus obtained.

C. *Proof of the Existence of Potassium Tri-iodide in Aqueous Solution.* The method of proof is the same here as in the above case. Place a few grams of finely powdered iodine in each of seven bottles, and add 250 c.c. of water to the first, 250 c.c. of $\frac{1}{128}$ normal KI to the second, 250 c.c. of $\frac{1}{64}$ normal KI to the third, 150 c.c. of $\frac{1}{32}$ normal KI to the fourth, 150 c.c. of $\frac{1}{16}$ normal KI to the fifth, 75 c.c. of $\frac{1}{8}$ normal KI to the sixth, and 75 c.c. of $\frac{1}{4}$ normal KI to the seventh. The concentration of these solutions must be accurately known, but the amount taken need only be roughly measured. Shake the seven bottles in a shaking-machine for about ten hours at as constant a temperature as possible. Let settle, and titrate 100 c.c. of the clear solution from each of bottles 1, 2, and 3, with thiosulphate; 50 c.c. each from bottles 4 and 5; 25 c.c. from bottle 6; and 20 c.c. from bottle 7. From these results the *molecular* concentrations of iodine, D and B, are obtained; the value of A is the original concentration of the potassium iodide solution used. If these values are introduced in the above mass-law equation, a constant value for K should be obtained, which at 20° is about 0.0013.

Experiments with more concentrated potassium iodide solutions show an increase in the values of the constant; this indicates the presence of higher poly-iodides.

71. Rubidium Iodine Tetrachloride, $Rb[ICl_4]$; Potassium Iodine Tetrachloride, $K[ICl_4]$; Rubidium Tri-iodide, RbI_3.

Dissolve 2.5 g. of rubidium chloride in 7.5 c.c. of water and suspend 2.7 g. of iodine in the solution. On passing chlorine into this mixture large, beautiful, orange-red crystals of rubidium iodine tetrachloride are obtained. The iodine dissolves during the action with a slight liberation of heat, and later the new salt separates in large plates which increase in quantity after several hours standing in the ice-chest. Drain the crystals without washing and allow them to dry for an hour in a vacuum desiccator over sulphuric acid. Too long drying causes decomposition. Yield about 5 g.

A corresponding potassium iodine tetrachloride is formed by triturating 1 g. of potassium iodate with a little concentrated hydrochloric acid in a mortar. Chlorine is liberated as the iodine of the iodate is reduced. Continue the trituration, adding small portions of concentrated hydrochloric acid from time to time, until finally there is no further evolution of chlorine. This requires about 5 c.c. of acid. A paste of dull-yellow crystalline needles remains. Filter, drain with suction and wash with a little concentrated hydrochloric acid. On standing, the salt slowly decomposes.

The behavior of this salt with ether, which dissolves out iodine trichloride and leaves behind white potassium chloride, would indicate that it may have the constitution $K[Cl \cdot ICl_3]$.

Rubidium Tri-iodide, RbI_3, is obtained by crystallization from a warm solution of iodine in rubidium iodide. Neutralize a solution of 2.5 g. of rubidium hydroxide in 3 g. of water with concentrated hydriodic acid, add 6.2 g. of iodine, and heat until solution is complete. On cooling, the salt separates in crystals resembling iodine. Treat them as in the preceding preparation.

(*d*) *Polynitrides.*

72. Sodium Hydrazoate NaN_3, from Sodamide $NaNH_2$.

Sodamide reacts with nitrous oxide to form sodium hydrazoate, the salt of hydrazoic acid, HN_3; from an aqueous solution of sodium hydrazoate, silver nitrate precipitates the difficultly soluble silver salt, a substance which like the pure hydrazoic acid is extremely explosive. Hydrazoic acid, or azoimide, was discovered by Curtius in 1890; the method of preparation given below was devised by W. Wislicenus, in 1892. The relationship between hydrazoic acid, iodo-hydriodic and brom-hydrobromic acids was pointed out by Hantzsch in 1895, as well as by others.

Sodamide. Place an aluminium boat containing about 3 g. of sodium (cf. Sodium Peroxide, No. 65) in a combustion tube; support the tube on a row burner and heat the sodium to 300–400° in a current of dry ammonia. Generate this gas by heating 100 c.c. of concentrated ammonia solution and dry it by passing through a tube containing soda-lime. Hydrogen escapes from the end of the combustion tube together with the excess of ammonia, and the mixture can be made to burn. Sodamide must be preserved in a well-stoppered bottle.

Sodium Hydrazoate. Place a porcelain boat containing 0.5 g. sodamide in a combustion tube which is inclosed in an asbestos chamber (Fig. 4, p. 3). Prepare nitrous oxide by heating 10 g. of ammonium nitrate in a small flask; dry the gas by passing it through a calcium chloride tube, and conduct it over the sodamide. Then heat the combustion tube to 250° until the reaction is finished, after which moist litmus paper is no longer turned blue by the escaping gases.

$$NaNH_2 + N_2O = NaN_3 + H_2O,$$
$$NaNH_2 + H_2O = NaOH + NH_3.$$

Silver Hydrazoate. Dissolve the sodium hydrazoate in 10 c.c. of water; a portion of the solution, when treated with a little ferric chloride, gives a deep brownish-red color. Acidify another and very small portion of the solution with nitric acid, add silver nitrate, collect the precipitate on a filter, wash it with water, alcohol and then ether, and while the filter is still moist with ether, tear it into several small pieces. After drying in the air the small amounts of the preparation adhering to the bits of paper will explode violently when heated or struck. It is very dangerous to prepare any larger amount of silver hydrazoate than that indicated.

Another simple method for obtaining silver hydrazoate is given by Sabanejeff. Heat gently 1.5 g. of hydrazine sulphate (No. 122) with 4 c.c. of nitric acid, *d.* 1.3, in a test-tube which isprovided with a gas exit tube bent at right angles. Pass the escaping gas into a little silver nitrate solution in a second test-tube; silver hydrazoate is obtained in the form of a white, curdy precipitate. Filter and test the salt as before, *but do not preserve it.*

OXYACIDS AND THEIR SALTS.

(*a*) *Cyanates.*

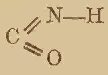
73. Potassium Cyanate; Urea from Ammonium Cyanate.

The cyanates, i.e. the salts of cyanic acid, are produced by the addition of oxygen to the cyanides:

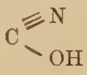
$$KCN + O = KCNO.$$

With regard to the constitution of cyanic acid there are two possible formulas:

I.



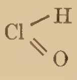
II.



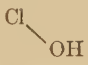
but which of these correctly shows the structure of the free acid and of its salts has not been definitely determined; it is quite possible that both forms exist in the presence of one another.

Similarly two possible formulas may be written for hypochlorous acid:

I.



II.



but the second is undoubtedly the correct one for free hypochlorous acid in aqueous solution.

The potassium cyanide required for the production of the cyanate is formed, together with some cyanate, by heating potassium ferrocyanide with an alkali:

$$K_4[Fe(CN)_6] + K_2O = Fe + KCNO + 5\ KCN.$$

In the presence of an oxidizing agent (CrO_3) the cyanide is oxidized to cyanate.

Dehydrate 130 g. of coarsely broken potassium ferrocyanide by stirring it in a shallow iron dish over a rather low Fletcher burner flame. When no more dark yellow particles can be detected in the lumps, grind the mass to a fine powder and remove the last traces of moisture by reheating. While still warm, triturate 100 g.

of the powder thus obtained with 75 g. of potassium dichromate which has been dried by being melted. Heat the mixture in the iron dish already used, whereupon the reaction will begin in spots and spread with incandescence throughout the mass. Pulverize the loose black product while still warm, cover it in a flask with a warm mixture of 450 c.c. 80% ethyl alcohol and 50 c.c. of methyl alcohol and boil it with a return condenser on the water bath for two minutes. Decant the hot solution through a plaited filter into a beaker, which is cooled with ice, and allow the salt to crystallize while stirring. Using the mother-liquor from this crystallization as a solvent, extract the black mass again in the same manner as before; filter, and repeat the extraction three or four times. Collect all of the cyanate crystals on the same suction filter, and after washing with ether, dry them in a vacuum desiccator over sulphuric acid. Yield, 30–40 grams. The product may be used in the preparation of urea, or of semicarbazid, No. 123.

Urea from Ammonium Cyanate.

Ammonium cyanate when heated in aqueous solution undergoes a transformation into urea (Wöhler, 1828).

$$NH_4CNO = CO(NH_2)_2.$$

To carry out this classic reaction, evaporate a solution of 8.1 g. potassium cyanate and 8.0 g. ammonium nitrate to dryness on the water bath. Boil the powdered residue in a flask twice with alcohol, and concentrate the extract until a crystallization in fine, long needles is obtained. Yield, about 5 g.

Heat a pinch of dry urea in a test-tube until it just melts, and keep it at this temperature for about a minute; ammonia escapes. Dissolve the residue in a little water and add a drop of copper sulphate solution and some sodium hydroxide, whereupon a rose-violet coloration appears; this is the so-called *biuret reaction*.

(*b*) *Oxy-halogen Acids.*

74. Electrolytic Production of Sodium Hypochlorite and Potassium Chlorate.

Sodium hydroxide and chlorine react in cold, aqueous solution, forming sodium hypochlorite, sodium chloride and water.

$$2\,NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

As soon as chlorine is present in excess, it reacts to produce free hypochlorous acid,

$$HOH + Cl_2 = HOCl + HCl;$$

and the latter being a much stronger oxidizing agent than sodium hypochlorite, or the hypochlorite ion, it oxidizes chlorite and hypochlorite ions into chorate ions:

$$2\ HClO + ClO^- = ClO_3^- + 2\ HCl,$$
$$3\ HClO + Cl^- = ClO_3^- + 3\ HCl.$$

Heating accelerates these reactions.

The raw materials necessary for these experiments can be prepared more conveniently by the electrolysis of alkali chloride solution than by purely chemical means. At the anode, chlorine is the primary product; sodium is the primary product at the cathode, but it immediately decomposes water to give sodium hydroxide and hydrogen. The products formed at the electrodes react together in the manner shown above when they are allowed to mix by diffusion.

The process as outlined above is, however, interfered with somewhat by the progress of certain secondary reactions. First, the hydrogen produced at the cathode reduces the hypochlorite, and to some extent the chlorate, to chloride. Since only the discharged hydrogen atoms, which have not yet combined to form molecules, cause the reduction, it is advantageous to restrict the formation of hydrogen to as small an area as possible; by this means the formation and escape of *gaseous hydrogen* is favored. In other words, the current density at the cathode must be kept high. To further avoid cathodic reduction, the deposition of a thin skin — a "diaphragm" — of hydrated chromic oxide on the metal of the cathode works excellently; this can be most simply accomplished by the electrolytic reduction of a little alkali chromate which is added to the electrolyte.

Second, the ClO^- and ClO_3^- ions, that are formed in the process, carry a part of the current, and when they become discharged at the anode, they then react with water to form the free acids and oxygen. The current which serves to discharge these ions is, therefore, wasted. The loss can be lessened by using a high anodic current density.

Both of these secondary reactions become more pronounced as the electrolysis progresses, i.e., as the concentration of the chlorate or the hypochlorate becomes greater. This explains why the yield for a given amount of current gradually grows less with a long-continued electrolysis.

Sodium Hypochlorite. A. The arrangement of the electrical connections, the external resistance, and the measuring instruments is that described in No. 14 (cf. Fig. 9). Place the beaker containing the electrolyte, which is a solution of 88 g. of sodium chloride in 500 c.c. of water (3-normal), inside a larger beaker containing ice water. For electrodes use two sheets of platinum of known area, e.g., 30 sq. cm. The anode reaches only into the upper part of the solution, the cathode nearly to the bottom with the attached wire insulated by being passed through a glass tube. The hydrogen bubbles rising from the cathode cause stirring. The current density should be the same at the anode as at the cathode and about 15 amperes per 100 sq. cm. of electrode surface (considering only one side of the electrodes, since it is chiefly between the inside surfaces that the current passes). The current strength holds fairly constant and does not need to be regulated much by changing the resistance. The minimum potential necessary for the electrolysis of a normal sodium chloride solution is 2.3 volts, but for obtaining the desired current density at least 6 volts will be required. The temperature of the electrolyte should not be allowed to exceed 20°. Follow the extent of the hypochlorite formation by an analysis every 10 to 20 minutes. For this purpose, remove 15 c.c. of the electrolyte with a pipette, let it stand in a beaker a short time until the gas bubbles have escaped, and then pipette 10 c.c. of it into a solution of potassium iodide which is slightly acid with hydrochloric acid. Titrate the iodine set free with 0.1-normal thiosulphate solution, and from the amount required calculate the entire amount of hypochlorite present in the whole solution. To determine the current yield,[1] find the total number of ampere-seconds used at the time of taking the samples, then calculate from this the theoretical yield, on the basis that 96,540 amperes flowing for one second would set free one equivalent each of sodium and of chlorine and thus produce one-half mol. of NaClO. The observed data and the calculated values can be arranged advantageously in a table as follows:

Time in Minutes.	Volume in c.c.	Temperature.	Amperes.	Theoretical Yield in Grams.	c.c. $Na_2S_2O_3$ Used.	Actual Yield in Grams.	Current Yield.
0	500	10	6.	0	0	0	0
10	500	11	6.6	—	—	—	—
20	500	13	6.3	2.91	12.6	2.34	80.4%
40	485	18	6.2	2.89	19.8	1.30	45.0%

Continue the electrolysis until the current yield falls below 30%, which may take about an hour, and calculate, from the last titration showing a yield better than 30%, the number of grams of "active" chlorine in a liter of the solution (7 to 9 g.).

B. Repeat the above experiment, using again 500 c.c. of 3-normal sodium chloride as the electrolyte, but adding to it 2.5 g.

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[1] Compare the data in No. 14.

of neutral sodium chromate. Before titrating with sodium thiosulphate, acidify strongly and dilute well, in order that the color of the chromate may not interfere with the end-point. From the total volume of thiosulphate used deduct the amount which corresponds to the iodine set free by the chromate. The current yield is now much better, on account of the addition of the chromate, and remains above 30% for a longer time; the total yield of "active" chlorine, computed as above, now amounts to from 14 to 16 g. per liter.

C. If experiment A is repeated without cooling the solution, the current yield falls very rapidly to below 30%, and the quantity of active chlorine produced before this point is reached amounts to only about 5 or 6 g. per liter.

Test qualitatively the bleaching action of the hypochlorite solutions obtained by adding a little to some indigo solution.

Potassium Chlorate. As electrolyte use a solution containing 100 g. of potassium chloride and 1 g. of potassium pyrochromate in 250 c.c. of water. Use a 600 c.c. beaker for the electrolyzing vessel, and cover it with the two halves of a divided watch glass. The electrodes should be, as before, of sheet platinum. Maintain at the anode a current density of 20 amperes per 100 sq. cm. and at the cathode a higher density. Keep the temperature at 40–60°, using a small flame if necessary to add to the heating effect of the current. A source of current at from 6 to 10 volts will suffice to maintain the necessary potential. Pass a slow stream of carbon dioxide continuously into the solution between the electrodes. To obtain a good yield, about 60 ampere-hours are required; thus for an anode surface (one side) of 25 sq. cm. the experiment must be continued 14 hours. If necessary it is permissible to interrupt the electrolysis. Occasionally replace the water lost by evaporation.

A little potassium chlorate crystallizes out during the electrolysis, but the main part is obtained after cooling; drain the crystals with suction and wash with a little cold water. To determine the entire yield of chlorate, dilute the mother-liquor to 500 c.c. and titrate a part of it with ferrous sulphate: boil 10 c.c. of the solution in a flask in order to drive out the free chlorine, replace the air by means of carbon dioxide, and after cooling add 50–70 c.c. of a 0.1-normal ferrous ammonium sulphate solution acidified with sulphuric acid. Close the flask with a Bunsen valve and boil the solution ten minutes. After cooling, dilute the liquid to twice its volume, add 20 c.c. of a 20% manganous sulphate solution to prevent the hydrochloric acid from interfering with the titration, and titrate in the cold with 0.1-normal potassium permanganate. A slight correction can be applied to allow for the chromate present. Determine in a similar manner the percentage of $KClO_3$ in the crystals obtained; then calculate the entire quantity of potassium chlorate and the current yield. It is to be remembered that according to the equation for its formation, 96,540 ampere-seconds yield but 1/6 of a mol. of $KClO_3$. The current yield amounts to about 70%, and about 85% of all the chlorate is obtained in the crystals. A further loss occurs when the crude, solid product is purified by recrystallization from hot water. The yield of purified chlorate actually obtained in an experiment carried out according to the above directions was 23 g.

The chlorate dissociates into a potassium ion and a chlorate ion. Test the purity of the preparation by dissolving a little in water, acidifying with nitric acid and adding silver nitrate; there should be no precipitate of silver chloride.

To illustrate the decomposition of chlorates by heat, melt a little of the preparation in a test-tube and test for oxygen with a glowing splinter (see the next preparation).

75. Potassium Perchlorate.

Potassium chlorate on being heated to about 400° decomposes in two different ways:

1. $4\,KClO_3 = KCl + 3\,KClO_4$.
2. $KClO_3 = KCl + 3\,O$.

If the vessel is clean and the potassium chlorate pure, the decomposition proceeds essentially according to equation 1. If, on the other hand, catalyzers are present, such as manganese dioxide or ferric oxide, or if it is heated to a higher temperature, then the reaction takes place principally according to equation 2. It is on this account that a mixture of manganese dioxide with potassium chlorate is used, rather than the pure chlorate, in preparing oxygen.

Heat 50 g. of potassium chlorate in a new 100 c.c. porcelain crucible until the salt just melts. Without increasing the heat keep the temperature as uniform as possible, so that oxygen barely escapes while the melt gradually becomes more viscous and pasty. If at the end of 10 or 15 minutes the mass has become uniformly semi-solid, allow it to cool, then cover it with 50 c.c. of cold water and allow it to stand until fully disintegrated. Collect the undissolved potassium perchlorate on a filter and recrystallize it from 200 c.c. of water. Yield, 30 g. The potassium chloride passes into the filtrates.[1]

Potassium perchlorate, like the chlorate, yields no precipitate with silver ions.

Heat in a dry test-tube a mixture of potassium chlorate and one-sixth of its weight of manganese dioxide, and test the oxygen evolved with a glowing splinter. Observe that the evolution of oxygen takes place at a lower temperature than when pure potassium chlorate is used. Extract the residue with water, and filter; potassium chloride is in the filtrate, as may be shown with silver nitrate.

Free perchloric acid is not explosive. Potassium perchlorate when covered with concentrated sulphuric acid remains unchanged in the cold and does not explode on gentle heating; potassium chlorate, on the other hand, yields explosive chlorine dioxide even in the cold. Pure perchloric acid, or a perchlorate mixed with concentrated sulphuric acid, must be handled with caution, since if it comes in contact with any oxidizable matter when warm it explodes with great violence.

76. Iodic Acid and Iodic Anhydride; a "Time Reaction."

Seal a 0.5–1.0 meter long glass extension tube to the neck of a round-bottomed flask, and boil 32 g. of iodine with 130 g. of concentrated, colorless nitric acid in the flask, using a ring burner to avoid bumping. Remove the lower oxides of nitrogen, as fast as they are formed, by means of a current of carbon dioxide, or of air. After the oxidation is complete and the solution has cooled, collect the solid iodic acid on an asbestos filter and separate it from the asbestos fibers by dissolving in the least quantity possible of hot water and filtering. Allow the iodic acid, HIO_3, to crystallize, after concentrating somewhat if necessary, by letting the solution stand in a vacuum desiccator over sulphuric acid. Evaporate the mother-liquor and dehydrate the residue at 200°. Iodic anhydride, I_2O_5, is thus obtained.

Heat a sample of the iodine pentoxide in a test-tube; it is broken down into iodine and oxygen, as is shown by the violet vapors and by the test with a glowing splinter.

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[1] At the room temperature about 36 g. KCl, 6.6 g. $KClO_3$, and 1.5 g. $KClO_4$ are soluble in 100 c.c. of water.

"Time Reaction."

If a solution of iodic acid is added drop by drop to an aqueous solution of sodium sulphite acidified with sulphuric acid, the solution at first remains colorless:

$$3\ H_2SO_3 + HIO_3 = 3\ H_2SO_4 + HI.$$

When, with further addition of iodic acid, all the sulphurous acid becomes oxidized, the reduction then continues at the expense of the hydriodic acid which has been formed:

$$HIO_3 + 5\ HI = 3\ H_2O + 3\ I_2.$$

Thus if an acidified sulphite solution is treated with more than one-third of a mol. of iodic acid, a separation of iodine occurs; if the solution is concentrated this takes place immediately; if dilute, only after some time, and then suddenly and completely.

This very remarkable retardation reminds one of the phenomena of supercooling, superheating, and supersaturation, but it is different inasmuch as the reaction takes place in a homogeneous medium, and is not followed by a separation of material in another state of aggregation.

Prepare one solution by dissolving 1.8 g. of iodic acid, or an equivalent amount of potassium iodate, in water and diluting to one liter; prepare a second solution with 0.9 g. of $Na_2SO_3 \cdot 7\ H_2O$, 5 g. of 10% sulphuric acid, and 9.5 g. of starch (the latter should first be suspended in a little cold water and then stirred into a beaker of boiling water to form a paste), and dilute this likewise to one liter. Measure 100 c.c. of each solution into separate beakers, mix these two portions at a definite instant, and count the seconds until a deep blue color suddenly appears. Check this result by repeating the experiment. Then dilute each of the solutions to $\frac{4}{5}$, $\frac{3}{5}$, $\frac{2}{5}$, and $\frac{1}{5}$ of their former concentrations, and determine for each dilution the time which elapses before the blue color appears. Plot graphically the dependence of the time on the dilution. The results are reproducible and comparable only when the temperature of the solutions does not vary appreciably.

77. Potassium Iodate from Potassium Chlorate.

$$2\ KClO_3 + I_2 = 2\ KIO_3 + Cl_2.$$

Place 30 g. of potassium chlorate in a 200 c.c. flask and dissolve it in 60 c.c. of warm water. Add 35 g. of iodine to the solution, and while maintaining the mixture at a moderate temperature introduce 1 to 2 c.c. of concentrated nitric acid. (Hood.) After one or two minutes a vigorous reaction begins and a stream of chlorine escapes, carrying with it a little iodine. When the reaction moderates, boil to drive off the chlorine, and, when this is nearly accomplished, add 1 g. more of iodine. Concentrate by evaporation until on cooling nearly all of the potassium iodate crystallizes; collect the product on a filter, and recover what is left in the mother-liquor by evaporation.

Dissolve the crude product, which always contains some acid salt, in 150 c.c. of hot water, and neutralize exactly with potassium hydroxide. On cooling a good yield of the pure salt is obtained.

Ignite a little of the product in a porcelain crucible, and test the residue for chloride by distilling it with potassium bichromate and concentrated sulphuric acid, and passing the vapors into ammonia water.

78. Potassium Bromate and Potassium Bromide.

To a solution of 62 g. potassium hydroxide in 62 g. of water, add 80 g. of bromine drop by drop while cooling by means of tap water. (Hood.) The solution soon becomes colored a permanent yellow, and later a crystalline powder of potassium bromate separates; after cooling completely, collect the bromate on a filter and purify it by recrystallization from 130 c.c. of boiling water. Combine all the mother-liquors and evaporate them to a semi-solid mass; mix this thoroughly with 5 g. of powdered wood-charcoal, dry it completely and then heat it to redness for an hour in a large porcelain crucible surrounded by an asbestos or sheet-iron funnel. Treat the sintered mass with 120 c.c. of hot water, and then wash the residue with 20 c.c. more of water; evaporate the filtered solution to crystallization. The yield is 26 to 27 g. of $KBrO_3$ and 90 to 95 g. of KBr.

The addition of acid to the aqueous solution of either one of these salts should not produce a yellow coloration, due to the separation of free bromine.

(c) *Nitrites and Nitrates.*

79. Sodium Nitrite from Sodium Nitrate.

Sodium nitrate, when melted with a reducing agent such as lead, loses one-third of its oxygen and goes over into the nitrite.

In the absence of reducing agents sodium nitrate can be melted without decomposition; at higher temperatures, however, a dissociation, although incomplete, takes place according to the equation:

$$NaNO_3 = NaNO_2 + O.$$

From the above facts the conclusion may be drawn that this dissociation of sodium nitrate takes place even at more moderate temperatures, although to so small extent that it can be proved only indirectly. The reducing agent by removing oxygen, one of the products of the dissociation, causes the decomposition to continue until it has become of appreciable magnitude. This is a good example of a non-electrolytic dissociation which though actually insignificant can be made apparent by the use of a reagent.

Sodium nitrite is the most important technically of all the salts of nitrous acid. It is used principally for diazotizing in the manufacture of azo-dyes.

Heat 85 g. of sodium nitrate in an iron dish, of 15 cm. diameter, until it melts, and add 207 g. of lead a little at a time while stirring with an iron spatula. Continue the heating until all the lead is oxidized, which may take half an hour, and then while cooling keep stirring in order to obtain the mass in small loose lumps. Extract the product first with 300 c.c. of hot water and then twice more with 100 c.c. To precipitate the lead which has gone into the solution as plumbite, pass in carbon dioxide for a few minutes. Filter and neutralize the filtrate cautiously with a very little dilute nitric acid. Evaporate to a small volume to obtain crystals, collect these on a suction-filter, wash with alcohol, and evaporate the mother-liquor to obtain more crystals. Yield, 40–50 g.

The lead oxide can be again converted into lead by reduction with charcoal (No. 1).

80. Potassium Nitrate from Sodium Nitrate.

If a mixture of sodium nitrate and potassium chloride is boiled with a quantity of water insufficient for complete solution, the undissolved residue will be sodium chloride, which is the least soluble in hot water of the four possible salts:

$$NaNO_3 + KCl \rightleftarrows KNO_3 + NaCl.$$

If the filtrate is cooled, potassium nitrate will crystallize, since this is the least soluble at the room temperature.

GRAMS OF SALT SOLUBLE IN 100 GRAMS OF WATER.

	At 10°.	At 100°.
Potassium nitrate......	21	246
Sodium chloride.......	36	40
Potassium chloride.....	31	56
Sodium nitrate........	81	180

Thus the interaction of the salts used depends entirely upon the solubility relations.

This method has had an important application in the manufacture of potassium nitrate for the gunpowder industry.

Dissolve 190 g. of crude Chile saltpeter in 200 c.c. of boiling water in a previously weighed flask. To the boiling solution add 150 g. of powdered potassium chloride and boil for half an hour longer, replacing any water lost by evaporation. The contents of the flask should at the end weigh 520 to 540 g. While still hot, filter rapidly through a Büchner funnel and rinse the residue with a test-tubeful of hot water. Cool the filtrate rapidly while shaking, whereby a crystalline meal of potassium nitrate is formed. Evaporate the mother-liquor; remove the sodium chloride by filtering while hot; and cool the filtrate rapidly to obtain more potassium nitrate. If sufficient mother-liquor still remains, work it up in the same manner to obtain a further yield. Unite all of the crystals of potassium nitrate and purify them by recrystallization until they are free from chloride. The yield is from 60 to 70% of the calculated.

81. Silver Nitrate.

The nitrates of the alkali metals break down into nitrites when heated; those of all the other metals dissociate into metallic oxide and nitric anhydride or its decomposition products:

$$Cu(NO_3)_2 = CuO + N_2O_4 + O.$$

This dissociation begins to take place at very different temperatures with the various metals. Silver nitrate can be melted without decomposition, while, at the same temperature, the nitrates of metals with a higher valence, for example, copper nitrate, are decomposed; thus by melting a mixture of these two nitrates and dissolving the fusion, silver nitrate can be obtained free from copper.

By carefully regulating the temperature and repeating the process, mixtures of very closely related nitrates can be separated; the "nitrate method" for separating the metals of the rare-earths depends upon this principle.

A completely analogous behavior is shown by the sulphates, as in the Ziervogel process for obtaining silver from argentiferous pyrite. By roasting, the sulphates of the metals are first formed, all of which, however, with the exception of silver sulphate, decompose at a somewhat higher temperature into metal oxide and sulphur trioxide; by leaching, the silver is obtained in the solution.

Dissolve a silver coin in 30% nitric acid, evaporate the solution to dryness, and transfer the residue to a porcelain crucible. Place this crucible upon a wire triangle inside a larger crucible, and gradually heat the outer crucible to a dull red heat. When the decomposition is completed, extract the black residue with water, concentrate the filtrate and test it for copper. Should any copper be present, which will frequently be the case, evaporate the solution to dryness and heat the silver nitrate carefully until it just begins to melt. In this way the remainder of the copper nitrate is decomposed. Repeat the extraction with water.

The copper oxide residues should contain very little silver.

82. Bismuth Nitrate and Basic Bismuth Nitrate.

Bismuth nitrate may be obtained from the solution of the metal in nitric acid in the form of large, colorless crystals with 5 molecules of water. The salt is strongly hydrolyzed by water, and, according to the temperature and the concentration of the acid, basic salts of various compositions are produced.[1] The following directions yield a precipitate of approximately the composition, $4\ Bi_2O_3 \cdot 3\ N_2O_5 \cdot 9\ H_2O$, which is not, however, to be regarded as a homogeneous compound. This is the so-called *bismuth subnitrate* so much used in medicine and often called *bismuth* by physicians.

Dissolve 100 g. of coarsely pulverized bismuth by heating it in a flask with 500 g. of nitric acid (sp. gr. 1.2). Filter through a hardened filter, using suction, and evaporate in a porcelain dish until crystallization begins. Collect the crystals on a suction-filter, wash with a little nitric acid (sp. gr. 1.2) and dry in a desiccator. Evaporate the mother-liquor to obtain more crystals.

To prepare the above mentioned basic salt, triturate one part of the bismuth nitrate with four parts of water and stir this mixture into 21 parts of boiling water. Allow the precipitate to settle, wash by decantation, collect on a suction-filter and dry the preparation at a temperature not exceeding 30°.

(*d*) *Manganates and Ferrates.*

83. Potassium Permanganate by the Fusion Method.

By fusing manganese compounds in an oxidizing-alkaline flux a manganate is formed, and this, when it is dissolved in water and the free alkali is neutralized, changes into permanganate and manganese dioxide:

$$MnO_2 + K_2CO_3 + O = CO_2 + K_2MnO_4,$$
$$3\ K_2MnO_4 + 2\ H_2O = MnO_2 + 4\ KOH + 2\ KMnO_4.$$

Melt together 80 g. of potassium hydroxide and 40 g. of potassium chlorate in a sheet iron crucible 6 to 8 cm. in diameter. Remove the flame and while stirring with an iron spatula (a heavy wire or an old file), add 80 g. of finely powdered pyrolusite, quite rapidly but not all at once. The fusion effervesces somewhat.

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[1] Cf. A. Findlay: The Phase Rule.

Heat again, at first moderately then more strongly, and stir vigorously all the while until the mass has become dry. Finally heat for 5 minutes at a dull red heat. Unless stirred as directed, the melt will solidify to a hard cake which can be removed from the crucible only with difficulty. When it is cold, break up the mass and boil it with 1.5 liters of water while conducting a vigorous stream of carbon dioxide into the liquid. When the manganate is completely decomposed and a drop of the solution gives a clear, violet-red spot on filter paper, with no trace of green, allow the precipitate to settle, and decant the liquid as carefully as possible from the sludge of manganese dioxide. Filter with suction through a felt of asbestos on a Büchner funnel. Concentrate the filtrate to one-half, filter again through asbestos, and evaporate until crystallization begins. Collect the crystals on a porcelain filter-plate and wash with a little cold water. Obtain a second crop of crystals from the mother-liquor and examine with a microscope to see if it is free from crystals of potassium chloride. Finally recrystallize. The yield should be 50 to 60 g. of the pure salt. The yield can be improved somewhat by using chlorine instead of carbon dioxide.

84. Electrolytic Preparation of Potassium Permanganate.

If a solution of an alkali hydroxide, or better of an alkali carbonate, is electrolyzed with an anode of manganese, permanganate is formed by anodic oxidation. For the reaction to succeed it must be carried out at a rather high temperature, since otherwise only manganate is formed. For the cathode, nickel or iron wires may be used, but they must be surrounded with a porous clay diaphragm to avoid reduction of the permanganate.

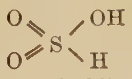
Place a porous cup, 10 cm. high and 4 cm. wide, in a liter beaker, and inside the cup place an iron wire to serve as the cathode. For the anode use a good sized lump of manganese (obtained by the Goldschmidt process; cf. No. 2); fasten it by means of a fine platinum wire to a stout iron wire and allow only the manganese to dip into the liquid. Use as the electrolyte 200 c.c. of a solution of potassium carbonate saturated at 0° (solubility: 105 g. of K_2CO_3 in 100 g. of water) which should stand at the same level inside and outside the porous cell. In order to effect a rapid electrolysis it will probably be necessary, on account of the high resistance of the diaphragm, to draw from a current supply of more than 6 volts. Raise the temperature of the bath to 50–60° and maintain it at this point by using an external flame whenever it is necessary to supplement the heating effect of the current. The formation of permanganate begins as soon as the current starts; red films of solution form at the anode surface and sink to the bottom of the beaker. At the end of 30 minutes, and then after every 20 minutes, stir the bath well and take samples of 5 or 10 c.c. with a pipette for the purpose of determining the current yield.[1] Acidify the sample with sulphuric acid, whereupon the precipitate, which is mainly ferric hydroxide, dissolves; decolorize the hot solution with a measured excess of 0.1-normal oxalic acid and titrate back at 60° with 0.1-normal permanganate. The permanganate solution obtained in this manner is so dilute that it does not pay to attempt to crystallize the solid salt. The current yield in several experiments made in the author's laboratory with 1.5–3.0 amperes was as high as 25% at the end of 45 minutes; in the next hour it sank to about 10%.

85. Barium Ferrate, $Ba[FeO_4]$.

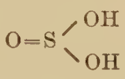
Clamp a 50–75 c.c. flask in an upright position and place in it a mixture of 10 g. of fine iron filings and 20 g. of potassium nitrate. Heat with a flame until a reaction takes place and the iron burns with a shower of sparks. After cooling break the flask, extract four times with 50 c.c. of ice water, and filter the combined extract through asbestos. Pass the deep violet-red filtrate again through a fresh asbestos felt and precipitate it immediately with a solution of barium chloride. After an hour drain the precipitate of barium ferrate on a hardened filter, wash it with alcohol, then with ether, and dry at the room temperature in a vacuum desicccator. Yield, 1.0 to 1.5 g.

(*e*) *Oxy-acids of Sulphur and Their Salts.*

For sulphurous acid the two following constitutional formulas[2] have been proposed:



Unsymmetrical Formula.



Symmetrical Formula.

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[1] Compare the directions in Preparations 14 and 74.

[2] Constitutional formulas of the complex inorganic acids apply only with a certain reservation: They characterize the ability to react only in one particular direction, and show, of several possibilities, only one definite condition of the acid (see cyanic and hypochlorous acids). They are of value, however, as aids to the memory.

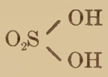
For a further discussion of these formulas, see Nos. 155 and 156.

Regarding the constitution of *sulphuric acid*, it is to be noted:

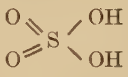
1. Sulphuric acid contains two hydroxyl radicals: sulphuryl chloride (No. 149) and water react together with the formation of sulphuric acid, whereby the chlorine atoms are replaced by hydroxyl groups:

$$SO_2Cl_2 \longrightarrow SO_2(OH)Cl \longrightarrow SO_2(OH)_2.$$

2. The two hydroxyl groups of sulphuric acid are bound to the sulphur atom: Either one or both of these groups can be replaced by organic radicals, such as phenyl, whereby phenyl sulphonic acid, $C_6H_5SO_2OH$, and diphenylsulphone, $(C_6H_5)_2SO_2$, are formed. But the same substances can be prepared by the oxidation respectively of mercaptan, C_6H_5SH, and of diphenyl sulphide, $(C_6H_5)_2S$, in which the organic radical must be joined directly to the sulphur atom. From this it follows that both hydroxyl groups are held by the same sort of a bond:



3. The way in which the two remaining oxygen atoms are bound is not known with certainty, but a mutual bonding of the two atoms to one another is improbable on account of the great stability of the SO_2-grouping. Thus the structural formula is apparently



Pyrosulphuric Acid, $HO.SO_2-O-SO_2.OH$, may be regarded as derived from two molecules of sulphuric acid by the loss of one molecule of water; it is prepared by dissolving sulphur trioxide in sulphuric acid.[1] By substituting the two hydroxyl groups of pyrosulphuric acid with chlorine atoms, pyrosulphuric-acid-chloride is obtained which is stable and easy to obtain pure. (See No. 150.)

Caro's Acid, $HO.SO_2.OOH$, is formed by the withdrawal of a molecule of water from between a molecule of sulphuric acid and a molecule of hydrogen peroxide.

Persulphuric Acid, $H_2S_2O_8$ (see No. 94), is produced by the electrolysis of H_2SO_4 when two discharged monovalent acid-sulphate anions, HSO_4, become united; it may also be regarded as resulting from the condensation of one molecule of sulphuric acid with one of Caro's acid.

Thiosulphuric Acid. Just as sulphuric acid may be formed by the addition of an atom of oxygen, so thiosulphuric acid, $H_2S_2O_3$, is produced by the addition of an atom of sulphur to a molecule of sulphurous acid (cf. No. 90).

Polythionic Acids. Among the polythionic acids are included *dithionic acid*, $H_2S_2O_6$, *trithionic acid*, $H_2S_3O_6$, *tetrathionic acid*, $H_2S_4O_6$, and *pentathionic*

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[1] Concerning the various hydrates of SO_3, see R. Knietsch, Ber. **34**, 4100 (1901). Notice particularly the curves.

acid, $H_2S_5O_6$. These can be prepared only in aqueous solutions or in the form of their salts. (Cf. Nos. 91, Barium Dithionate, and 92, Sodium Tetrathionate.) The acids readily change into one another, and their constitution is doubtful.

HYPOSULPHUROUS ACID, $H_2S_2O_4$. See No. 93.

86. Sulphuric Acid from Pyrite by the Chamber Process.[1]

Construct the apparatus shown in Fig. 20. The wide-mouthed liter bottle is closed with a cork through which three holes are bored. In one hole the bent-side arm of a 25 c.c. distilling flask is inserted. A delivery tube is passed through the second boring to the middle of the bottle and on the outside is joined to a short combustion tube. In the third boring a tube is inserted which leads through the safety bottle to a suction pump. Charge the combustion tube with about 10 g. of powdered pyrite, and place a small, loose plug of asbestos just beyond the powder to retain any unburnt sulphur. Place about 10 c.c. of concentrated nitric acid in the distilling flask, and insert a glass tube through the stopper so that the lower end, which is drawn out to a capillary, reaches to the bottom. Half fill the safety bottle with water to show the

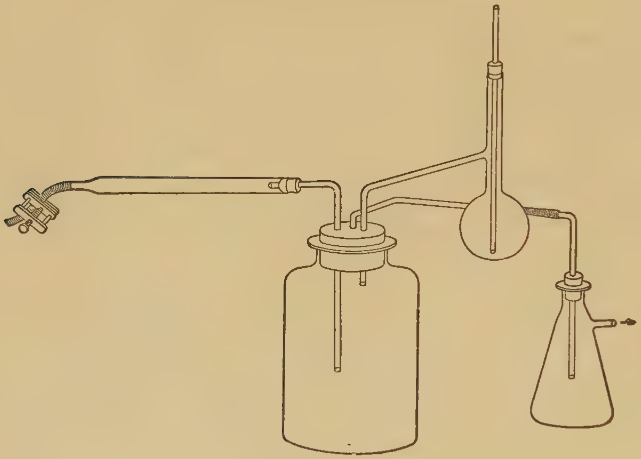

FIG. 20.

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[1] From Alexander Smith and William J. Hale's *A Laboratory Outline of General Chemistry*.

rate at which air is drawn through the apparatus. The total air admitted is regulated by a screw clamp placed between the safety-bottle and the water-pump, and the proportion passing over the pyrite and through the nitric acid is governed by the clamp shown at the end of the combustion tube.

First heat the pyrite in a slow stream of air until it takes fire. Then warm the nitric acid and, by partially closing the clamp at the end of the " pyrite-burner," cause air to enter also through the capillary in the distilling flask, and thus carry nitric acid vapors into the large bottle. Heat the pyrite strongly and continuously; regulate the current of air laden with nitric acid so that red fumes are always present in the bottle. If insufficient nitric acid is provided, the walls of the flask become coated with colorless crystals of nitrosyl sulphuric acid (" chamber crystals "; cf. No. 152).

When the pyrite is completely burned, disconnect the apparatus, and wash the contents of the bottle into a beaker with a little water. Test the solution qualitatively, and determine by titration the yield of sulphuric acid.

87. Reduction of Barium Sulphate and Preparation of Barium Nitrate.

Mix thoroughly 47 g. of finely powdered heavy spar with 12 g. of fine sifted charcoal, and place the mixture in a Hessian crucible which should be two-thirds to three-quarters filled by it. Spread a layer of charcoal on top, and place a cover on the crucible. Heat to a red heat for two hours in a charcoal furnace. After cooling break up the reddish-gray, porous contents of the crucible, and add it little by little to 600 c.c. of a solution containing 25 g. of nitric acid. Boil, filter, and evaporate the solution to crystallization. Separate the crystals on a filter, wash them with a little water, and dry them at a moderate temperature on a porous plate. Recover more crystals from the mother-liquor. Yield, 45 to 50 g. of $Ba(NO_3)_2$.

88. Antimony Sulphate $Sb_2(SO_4)_3$.

Antimony sulphate is an example of a salt which is very easily hydrolyzed. In spite of the fact that it can be crystallized from concentrated sulphuric acid, it is impossible to obtain it pure without adopting some special expedient. The sulphuric acid adhering to the crystals cannot be removed by suction or by evaporation. Washing with anhydrous acetic acid is effective, however, because this solvent does not react appreciably with either sulphuric acid or antimony sulphate, and the excess can be easily removed.

Add 10 g. of finely powdered antimony (from No. 7 or 10) in small portions to 100 c.c. of hot, concentrated sulphuric acid, and heat the mixture in a beaker nearly to boiling until all the antimony has dissolved. On cooling, antimony sulphate crystallizes in long, colorless, lustrous needles. Allow the solution to cool completely, dilute it with 80 c.c. of anhydrous acetic acid, and again permit the mass to cool. Drain the crystals by suction on a hardened filter, and wash them rapidly with a little anhydrous acetic acid and then with ether; allow the product to dry for one or two days in a vacuum desiccator over sulphuric acid. Yield, 13 g.

If a sample of the salt is treated with water, it undergoes hydrolysis, and free sulphuric acid is found in the solution decanted from the insoluble basic salt.

For the quantitative analysis of the salt, dissolve a weighed sample in a little concentrated hydrochloric acid, add tartaric acid, dilute well, and precipitate with barium chloride. From a second solution prepared in the same way, precipitate the antimony with hydrogen sulphide and weigh it in a Gooch crucible as Sb_2S_3 after drying it in an atmosphere of carbon dioxide at 280°.

89. Alum from Kaolin.

Potassium aluminium sulphate, $K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O$, is distinguished from other aluminium salts by its marked ability to crystallize, and on this account it can readily be obtained pure. Thus it has long been the most important salt of aluminium in spite of the fact that it contains but 5.71% of that element. More recently, however, aluminium sulphate has been used a great deal instead of alum; it is prepared by neutralizing with sulphuric acid the hydrated aluminium oxide, which can now be prepared pure from the mineral bauxite.

Stir 50 g. of powdered kaolin with 75 g. of concentrated sulphuric acid in an evaporating dish; heat the mixture for 2½ hours on a Babo funnel, at first gently and then more strongly, until white fumes escape. Triturate the mass when cold, and extract once with 300 c.c. and then three times with 100 c.c. of boiling water; the last filtrate should show no test for aluminium with ammonia. Dissolve 28 g. of potassium sulphate (15% less than the calculated amount) in the combined filtrates, and bring the double salt to crystallization in the usual way. Recrystallize the combined crops of crystals. Yield, about 150 g.

90. Sodium Thiosulphate, $Na_2S_2O_3 \cdot 5\,H_2O$.

Add 16 g. of finely powdered roll sulphur (not flowers of sulphur) to a solution of 126 g. crystallized sodium sulphite, $Na_2SO_3 \cdot 7\,H_2O$, in 250 c.c. of water, and boil the mixture in a flask until, at the end of about two hours, the sulphur has dissolved. Filter, evaporate to the point of crystallization, and concentrate the mother-liquor to obtain further crops of crystals. The yield is nearly quantitative.

126 124,1 56.

The above reaction, $Na_2SO_3 + S \rightleftarrows Na_2S_2O_3$, is reversible. Heat 2–3 g. of sodium thiosulphate with about 5 g. of copper powder in a test-tube so that the thiosulphate melts in its water of crystallization and the latter partly boils away; the copper becomes black (copper sulphide), and the aqueous extract when treated with calcium chloride gives a precipitate of calcium sulphite; calcium thiosulphate is easily soluble.

248,19

91. Barium Dithionate, $BaS_2O_6 \cdot 2\,H_2O$.

Prepare sulphur dioxide by allowing sulphuric acid to drop into 160 c.c. of commercial bisulphite liquor (see note on p. 71), and pass the gas into a suspension of 50 g. of finely powdered pyrolusite in 250 c.c. of water until the latter is saturated and nearly all of the black manganese dioxide has dissolved. During this reaction, which lasts about two hours, keep the mixture cooled with water.

Dilute to 1.5 liters, bring the solution to boiling, and keep it at this temperature while adding a solution of 200 g. of crystallized barium hydroxide. Filter, and test the filtrate with ammonium sulphide for manganese. If the manganese is shown to be all precipitated, remove the excess of barium hydroxide from the filtrate by passing carbon dioxide into the boiling solution. Filter, evaporate to one-half, filter again, and allow the salt to crystallize. Drain the crystals and evaporate the mother-liquor to obtain another crop. Yield, about 120 g.

A sample of the salt dissolves clear in water and remains unchanged upon the addition of a little nitric acid. By boiling with nitric acid, however, it is oxidized to sulphate, and oxides of nitrogen are evolved.

92. Sodium Tetrathionate, $Na_2S_4O_6 \cdot 2\ H_2O$.

Triturate 50 g. of sodium thiosulphate, 26 g. of iodine, and 5 g. of water in a mortar to a bright brownish-yellow paste. After a short time rinse the mass with 50 c.c. of alcohol into an Erlenmeyer flask. At the end of about three hours drain the precipitated sodium tetrathionate and wash it with alcohol until the washings are free from iodine.

Dissolve the crude product in 20 to 25 c.c. of lukewarm water, and by adding alcohol in portions of 10 c.c. — in all 50 c.c. — bring about a separation of crystals. After about ten hours, during which time the mixture has stood out of contact with the air in an Erlenmeyer flask, or in a vacuum desiccator, drain the crystals, wash with alcohol, and dry in a desiccator over sulphuric acid. The yield is about 20 g. of compact, colorless, crystalline aggregates.

Reactions: A solution prepared in the cold gives no precipitate with copper sulphate even on boiling; with mercuric nitrate a yellow precipitate is obtained which becomes black on boiling; with mercuric chloride a yellow flocculent precipitate separates slowly. Compare the behavior of sodium thiosulphate and sodium sulphite with these reagents.

Analysis: Determine the water of crystallization in a 0.7–1.0 g. sample by heating it to constant weight in the steam closet; determine the sulphur by dissolving in water, oxidizing with bromine, and precipitating with barium chloride. The amount of water contained in the salt prepared in this way is stated variously in the literature.

93. Hyposulphurous Acid, $H_2S_2O_4$.

Zinc dissolves in aqueous sulphurous acid without evolution of hydrogen, and forms a yellow solution of great reducing power. By studying the properties of this solution and later by preparing the solid sodium salt, the formula of free hyposulphurous acid was established as $H_2S_2O_4$.

The older name for hyposulphurous acid is *hydrosulphurous acid.* It should not be confused with thiosulphuric acid, $H_2S_2O_3$, the sodium salt of which is commonly known as "hypo."

Take two samples of the same solution of sulphurous acid, allow one of them to stand a short time in contact with a zinc rod, and afterward test the reducing power of each solution towards dilute indigo.

94. Potassium Persulphate, Electrolytically.

In concentrated solutions of acid sulphates, dissociation takes place for the most part only partially:

$$KHSO_4 \rightleftarrows K^+ + HSO_4^-.$$

On electrolyzing, and particularly with high-current densities, the acid sulphate ions on becoming discharged at the anode unite in pairs to form persulphuric acid, $H_2S_2O_8$, the potassium salt of which is insoluble.

Inside a large beaker filled with ice water, place a glass cylinder, or a small beaker 14 cm. high and 6 cm. in diameter. Suspend in this, by means of a wire triangle, an 11 cm. long, 2.7 cm. wide glass tube open at both ends (a test-tube with its bottom cut off). Use for the cathode a loop of platinum wire, placed as near the surface of the solution as possible and outside the inner tube; for the anode melt a platinum wire into a glass tube so that it projects 1.5 to 2.0 cm., and insert this through the inner tube until it reaches nearly to the bottom of the beaker (see Fig. 21).

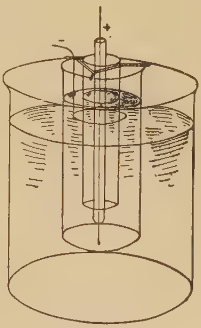

FIG. 21.

Fill the inside beaker one-half full of a saturated solution of acid potassium sulphate. Use a current density at the anode of 100 amperes per 100 sq. cm. of electrode surface. Measure the protruding anode wire and estimate its surface. The current will amount to less than an ampere with a moderately stout platinum wire. The temperature of the electrolyte should be lower than 15° and may quite easily be maintained at 6° to 8°. A few minutes after closing the circuit, crystals of the difficultly soluble persulphate are seen to separate. Continue the electrolysis 40 minutes in one experiment and an hour in another. Collect the salt on a hardened filter, wash it with alcohol and then with ether. Weigh the salt, after drying in a desiccator, and analyze it as soon as possible in the following manner: Dissolve 0.3 g. of the salt in a beaker with 10 c.c. of 0.1-normal ferrous ammonium sulphate[1] solution and 200 c.c. of hot water. After cooling, titrate back the unoxidized ferrous salt with 0.1-normal permanganate.

According to the above directions, 1.25 g. of the persulphate of 92 to 95% purity should be obtained in 40 minutes and 1.65 g. in an hour, and the current yield should be from 41 to 43%.

To test qualitatively the oxidizing power of the salt, dissolve some of it in water, make the solution alkaline, add it to a solution of a lead or manganese salt to which alkali has also been added, and heat the mixture.

(*f*) *Carbonates.*

95. Sodium Carbonate (Ammonia-Soda Process).

From a concentrated solution containing the ions Na^+, Cl^-, NH_4^+, and HCO_3^-, sodium bicarbonate, $NaHCO_3$, the most insoluble of the possible salts, is the first to separate (cf. No. 80). 100 grams of saturated aqueous solutions of the four salts that come into consideration contain the following weights of anhydrous salt in grams.

	15°	30°
NaCl	26.4	26.5
NH_4HCO_3	15.7	21.3
NH_4Cl	26.1	29.3
$NaHCO_3$	8.1	9.9

The dry acid salt loses carbon dioxide when heated and changes into the monocarbonate, Na_2CO_3. This process, which was first placed on a commercial basis by Solvay, yields at the present time the largest part of the world's soda. For a technical discussion of the process, consult Ost, Lehrbuch der technischen Chemie; for a theoretical treatment in the light of the phase rule, see Bodländer and Breull, Z. angew. Chem. **14,** 381, 405 (1901); and P. P. Fedotieff, Z. physikal. Chem. **49,** 162 (1904).

Add 60 g. of pulverized sodium chloride to 180 g. of a 10% ammonia solution, and allow it to stand with occasional shaking until nearly all has dissolved. Place the filtered solution in a closed flask and saturate it at room temperature with carbon dioxide; pass the gas through a wash bottle containing water and then allow it to enter the flask through a single inlet tube, which dips under the solution, as rapidly as it will be absorbed (in all, perhaps 24 hours).[2] Collect the precipitated sodium bicarbonate on a filter and wash it with a little cold water. Dry the product in a porcelain dish and then heat it with a free flame until carbon dioxide ceases to escape. Recrystallize the crude sodium carbonate thus obtained from five times its weight of water, and wash the crystals with a little water. Concentrate the mother-liquor to obtain another crop of crystals. Recrystallize. Yield, about 40 g.

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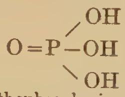
[1] 40 g. of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$ and 30 g. of conc. H_2SO_4 made up to 1 liter and standardized against 0.1-normal permanganate.

[2] The time taken for the absorption may be reduced to one-half hour if a 2 liter flask is used and it is shaken vigorously throughout the absorption.

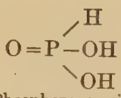
A solution of the sodium carbonate, after being acidified with nitric acid, ought not to show more than a slight cloudiness with silver nitrate.

(*g*) *Phosphoric Acids.*[1]

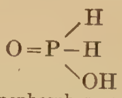
Structural formulas can be written as below for *orthophosphoric acid*, H_3PO_4, *phosphorous acid*, H_3PO_3, and *hypophosphorous acid*, H_3PO_2, if it is taken into consideration that the first acid is tribasic, the second dibasic, and the third monobasic, and if it is assumed, although this is by no means proved, that all the hydroxyl hydrogens, and only these, can be replaced by metals in the formation of salts.



Orthophosphoric acid.



Phosphorous acid.

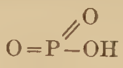


Hypophosphorous acid.

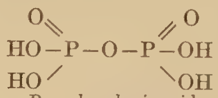
The reducing action of the last two acids would accordingly consist in taking up oxygen which would enter between the phosphorus atom and the hydrogen atoms.

If it is not assumed that all the hydroxyl hydrogens are replaceable, then the formulas $P(OH)_3$ and $HP(OH)_2$ become possible, according to which phosphorous and hypophosphorous acids are derived from tervalent phosphorus. It may be, as in the case of sulphurous acid, that both formulas have a certain justification (compare p. 126 and Nos. 155 and 156).

By the loss of water from one and from two molecules of orthophosphoric acid, *meta-phosphoric* and *pyro-phosphoric* acids respectively are obtained:



Metaphosphoric acid.



Pyrophosphoric acid.

Hypophosphoric Acid, H_2PO_3, which was formerly written $H_4P_2O_6$, has recently been found to have a molecular weight corresponding to the smaller molecule, and is presumably derived from quadrivalent phosphorus.

96. Barium Hypophosphite, $Ba(H_2PO_2)_2 \cdot H_2O$.

Salts of hypophosphorous acid are formed by the action of phosphorus on warm, aqueous solutions of strong bases:

$$4\,P + 3\,KOH + 3\,H_2O = 3\,KH_2PO_2 + PH_3.$$

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[1] Cf. Note 2, p. 126.

If barium hydroxide is chosen as the base, it is possible to obtain the crystallized salt, after precipitating the excess of the base with carbon dioxide and evaporating the filtrate. Hypophosphites are strong reducing agents.

Heat a solution of 120 g. crystallized barium hydroxide in 1200 c.c. of water with 30 g. of yellow phosphorus (Caution) in a round-bottomed flask on a Babo funnel. After about four hours nearly all of the phosphorus will have disappeared. The process should be carried out in a well-ventilated hood, since phosphine gas escapes freely. Filter the solution through a plaited filter into a large porcelain dish; heat and pass in carbon dioxide until the excess of barium hydroxide is precipitated. Filter, rinse the precipitate with boiling water, and evaporate the solution to one-half its volume. After again filtering, concentrate further — at the last in a beaker — until crystals begin to separate; then add alcohol and leave the solution to crystallize. Collect the product on a filter and evaporate the mother-liquor to obtain more crystals. Purify the entire product by recrystallization. Yield, 40 to 60 g. of colorless flaky crystals.

Reactions: 1. Treat a sample of the product with concentrated sulphuric acid and heat it to boiling; a large amount of sulphur dioxide escapes and sulphur distils to the cooler part of the test-tube.

2. On adding hypophosphite to a dilute solution of gold chloride, $H[AuCl_4]$, and warming gently, a blue-violet coloration (cf. No. 25) and later a violet-red precipitate of gold is obtained.

3. With silver nitrate a dark brown separation of silver takes place, slowly at the room temperature and more rapidly when warm; with mercurous salts a separation of mercury occurs.

4. If a dry sample of barium hypophosphite is heated in a test-tube, it turns red with loss of water and further decomposition: phosphorus distils off and phosphine escapes.

Dependent preparation: Copper Hydride, No. 33.

97. Phosphorous Acid.

Phosphorous acid, which is sometimes used in quantitative analysis, is prepared by the hydrolysis of phosphorus trichloride (No. 46):

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$

Pour 100 c.c. of water into a 200 c.c. beaker, place the beaker in ice water under the hood, and slowly add 25 g. (15 c.c.) of phosphorus trichloride from a dropping funnel. After the reaction is over, transfer the liquid to a distilling flask and distil off the hydrochloric acid and water under reduced pressure (p. 8). The phosphorous acid remains behind as a colorless, fibrous, crystalline mass which is hygroscopic and therefore must be kept in well stoppered vessels.

THIO-ACIDS AND THEIR SALTS.

98. Potassium Trithiocarbonate Solution (Reagent for Nickel).

Divide 50 c.c. of a 5% solution of potassium hydroxide into two equal portions; saturate one with hydrogen sulphide and mix it with the other portion. Shake this solution of potassium sulphide vigorously with 2 c.c. of carbon bisulphide for five minutes and then pour it through a filter which has been moistened with water. The bright, orange-red solution contains K_2CS_3, and is an extremely delicate reagent for nickel. With concentrated ammoniacal solutions of nickel salts, it gives a brownish-black precipitate; with dilute solutions, a dark brown coloration.

Determine the sensitiveness of the test: Start with 1 or 2 c.c. of a 0.0002-normal nickel solution, and if this gives a distinct reaction, dilute ten times and test again, and continue in this way until the limit of sensitiveness is reached.

In order to find to what extent cobalt interferes with the reaction, test solutions containing 1, 2, 10, 50 and more atomic equivalents of cobalt for each atom of nickel.

99. Barium Trithiocarbonate.

Dissolve 32 g. of crystallized barium hydroxide in 100 c.c. of hot water. Place one half of the solution in a closed flask and saturate it with hydrogen sulphide, whereby barium sulphydrate is formed; then add the other half of the original barium hydroxide solution. Shake the resulting solution of barium sulphide with 8 g. of carbon bisulphide, whereupon barium trithiocarbonate, $BaCS_3$, precipitates as a yellow, crystalline powder. Drain the precipitate, wash it with a little water, then with 50% alcohol, and finally with pure alcohol; and dry it in a warm place (on top of the hot closet). As the alcohol used for washing runs into the filtrate, more of the barium trithiocarbonate precipitates. Yield, 12 to 15 g.

100. Sodium Thioantimonate, $Na_3SbS_4 \cdot 9\ H_2O$.

Sodium thioantimonate, or "Schlippe's salt," is formed by the interaction of antimony sulphide, sodium sulphide, and sulphur; sodium thioantimonite may first be formed in the dry way (Schlippe), or the whole process may be carried out in the wet way (Mitscherlich). According to Schlippe's method, sodium sulphate is heated together with charcoal and antimony trisulphide in the furnace; sodium sulphide is formed by reduction, and this immediately combines with the antimony sulphide. By suspending the pulverized fusion in water and boiling it with powdered sulphur, the sodium thioantimonite is converted into thioantimonate.

In recrystallizing the salt, it is necessary to add a little sodium hydroxide to prevent hydrolysis, for otherwise the free thioantimonic acid which would form would decompose into antimony sulphide and hydrogen sulphide. Sodium thioantimonate is used in making the medicinal preparation of antimony pentasulphide.

1. Mix thoroughly 36 g. of powdered stibnite (34 g. = 0.1 mol.), 43 g. of anhydrous sodium sulphate, and 16 g. of powdered charcoal. Place the mixture in a Hessian crucible, which should be about half filled, cover with a layer of charcoal, and heat in a charcoal furnace until the charge comes to a state of quiet fusion, and then heat ten minutes longer. Pour the melt upon an iron plate, pulverize the mass when cold, and boil it half an hour with 7 g. of flowers of sulphur and 300 c.c. of water. Add a little caustic soda solution and evaporate the filtrate to crystallization in a porcelain dish. Collect the crystals, wash them with a little alcohol, and work up the mother-liquor further. Recrystallize the combined portions, adding a little caustic soda to the solution; dry the product in a vacuum desiccator over lime, upon which a few drops of ammonium sulphide have been poured. The yield is 40 to 50 g. of light-yellow well-formed crystals.

2. Slake 26 g. of quicklime with hot water, stir it up to a paste with an additional 80 c.c. of water, and add a solution of 70 g. crystallized sodium carbonate in 250 c.c. of water. Bring the mixture to boiling in an iron dish, and while it is boiling add little by little a paste made from 36 g. of powdered stibnite, 7 g. of powdered sulphur, and 12 g. of water. When, after boiling about 15 minutes, the gray color of the antimony sulphide has disappeared, filter the solution through linen cloth and extract the residue by boiling it with 100 to 150 c.c. of water. Bring the

combined filtrates to crystallization and proceed as in Method 1 with the recrystallization, etc. Yield, about 60 g.[1]

101. Potassium Ferric Sulphide, $K[FeS_2]$.

Place an intimate mixture of about 30 g. iron powder, 180 g. flowers of sulphur, 150 g. potassium carbonate, and 30 g. anhydrous sodium carbonate in a Hessian crucible, and heat the mass in a charcoal furnace until it is melted to a thin liquid. This takes about an hour. Close the furnace and let the melt cool slowly; break the crucible and digest the lumps of the melt with warm water in a porcelain dish until they are completely disintegrated. From time to time replace the resulting green solution with fresh water until nothing more dissolves and pure, glistening, dark needles remain behind. Wash the product with water and alcohol and dry it in the steam closet. Yield, about 70 g. Confirm the composition by a quantitative analysis. The experiment can be performed on a smaller scale using about one-sixth as much of each substance. In this case a porcelain crucible and a blast lamp or Méker burner should be used.

102. Ammonium Copper Tetrasulphide, $NH_4[CuS_4]$.

It is known from qualitative analysis that copper sulphide dissolves appreciably in ammonium or sodium polysulphide. Alkali salts of thio-copper acids are thereby formed of which the one under consideration has been best investigated.[2]

Place a mixture of 200 c.c. of concentrated ammonia and 50 c.c. of water in a closed flask, and while keeping the liquid cooled with tap water, pass in hydrogen sulphide until it is saturated. Dissolve in one-half of the solution as much finely powdered sulphur as possible at 40° (about 60 g.), then filter this and add it to the other half of the solution.

While rotating this solution in a flask, add a 10% solution of blue vitriol little by little until a permanent precipitate of copper sulphide just begins to form; filter immediately through a plaited filter into an Erlenmeyer flask; the latter should be filled almost completely with the liquid. On standing, best in an ice-box, brilliant red prisms separate, which on the next day should be washed with water and then with alcohol and dried quickly over lime in a vacuum desiccator. On adding copper sulphate to the main filtrate (to which the washings should not have been added) a further yield of the crystals is obtained. The entire product is about 25 g.

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[1] The yield corresponds closely with the reaction as given by Mitscherlich: $8\,Sb_2S_3 + 16\,S + 18\,Na_2CO_3 + 3\,H_2O = 10\,Na_3SbS_4 + 3\,H_2Na_2Sb_2O_7 + 18\,CO_2$.

[2] H. Biltz and P. Herms, Ber. **40,** 977 (1907).

A sample of the salt dissolves completely in a small amount of 2-normal sodium hydroxide, which points to the existence of the copper as a part of the complex; after some time copper sulphide begins to separate slowly. Ammonia is readily detected in this solution by its odor or by Nessler's reagent. Concentrated potassium hydroxide added to the fresh solution immediately precipitates red potassium copper tetrasulphide. Concentrated hydrochloric and nitric acids act but slowly on the dry salt, concentrated sulphuric acid not at all.

COMPLEX HALOGEN ACIDS AND THEIR SALTS. — COMPLEX CYANOGEN COMPOUNDS.

Among the complex compounds formed by the union of two simple substances, the particular class in which both of the simple substances are halogen or cyanogen compounds requires a special treatment, — first, for the reason that the number of such compounds is very great, and many of them are of considerable practical importance; and second, because their classification and interpretation on the basis of the old theories of valence have for a long time caused chemists much perplexity.

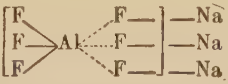
For the diagnosis of such complex compounds, purely chemical tests are first made as to the reactivity of their constituents. If the typical reactions of the simple salts do not occur with these double compounds, but instead new specific reactions are found, then a complex structure of the substance is indicated. Such cases are abundant in analytical chemistry, as, for example, with the iron-cyanogen compounds.

Further, the existence in aqueous solution of complex metal-containing ions can be proved electrochemically, and with this proof began the clearing up of the constitution of these substances. The metal migrates, as a constituent of the anion, toward the positive pole and there increases in concentration. Thus an anomalous change in concentration takes place with respect to the metal when it is compared with that occurring in the electrolysis of simple metal salts. From this Hittorf, in the years 1853–1859, deduced the existence of complex ions in solution. Previously Porett (1814) had noticed, incidentally, the analogy existing between potassium ferrocyanide and the salts of the oxy-acids.

Finally, the degree of the complexity of dissolved double compounds can be estimated by means of any one of the methods of determining ion concentrations, such as by measurements of the freezing-point, of electromotive force, etc. Thus not only can the extreme cases be distinguished — in which there is merely a dissociation into a simple cation and a complex anion or else a complete breaking down into the simple ions — but also it can be shown, in the transition cases, to what degree the two kinds of dissociation prevail.

The extent to which the nature of the compound, and indeed the nature of the elements forming the complex as well as of those outside of the complex, favors the first or second form of dissociation is now understood in a general way. The formation of complexes seems to be favored when the anions of the simple compounds are the same. The stability of the complex increases from the chlorine compounds through the other halogen to the cyanogen compounds; it increases further, as far as metal-containing anions are concerned, with the "nobleness" of the metal. The latter property of metals is intimately connected with the discharge potential of their ions — a quantity capable of exact measurement — (electroaffinity, cf. p. 67), hence it would seem possible to predict, from data concerning discharge potentials, the relative tendency of the metals to form complexes. Abegg and Bodländer have in fact proposed a new system of chemical classification[1] based upon this fundamental property of the atoms. Among the numerous investigations which these ideas have instigated, mention should be made of the measurements carried out by Bodländer of the so-called "stability-constants" which give the proportion in which simple metal ions dissociate from complex metal-containing anions.[2]

The composition of the complex halogen compounds shows that one atom of non-haloid nature occupies a peculiar position in the complex, while the remaining atoms of the complex, which are either all of the same kind or closely related, are most frequently either four or six in number. Starting from these facts Werner has used with success the so-called "Coördination Theory,"[3] which he himself proposed, to explain the constitution of these compounds. According to this theory the halogen atoms are situated in space around the other atom of the complex, the "central atom"; when they number four they may be supposed to be located at the corners of a tetrahedron, and when they number six, at the corners of an octahedron which surrounds the central atom (see p. 166). Werner has, in constructing his theory, also introduced the idea of "secondary valences" which differ from the "principal valences" by being weaker and incapable of binding electrons. Thus aluminium, when its three principal valences are saturated with fluorine, can bring into play its three secondary valences, and thereby bind the fluorine atoms in three molecules of sodium fluoride:



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[1] Abegg and Bodländer: Die Electroaffinität. Z. anorg. Chem. **20**, 453 (1899).

[2] Bodländer: Ber. **36**, 3933 (1903).

[3] For a full discussion of this theory see A. Werner, Neuere Anschauungen auf dem Gebiete der anorganischen Chemie, 4th Edition, 1919.

The secondary valences have nothing to do with the state of oxidation of the central atom, which is determined by the primary valence alone. Thus in tervalent cobaltic salts, the element cobalt acting as a central atom tends to unite with six other atoms, radicals or molecules. In the $[Co(NH_3)_6]^{+++}$ ion, therefore, the 6 molecules of NH_3 are held in place by secondary valence bonds and the ion has the triple charge because none of the principle valences are satisfied in the complex cobalt-ammonia ion. In $[Co(NO_2)_6]^{---}$, the NO_2 radicals have a negative valence of one; the 6 NO_2^-, therefore, neutralize all of the primary valences of the cobalt and since there are only three of these, the anion has a negative valence of $6 - 3 = 3$. The primary valences are characteristic of the element and its position in the periodic classification of the elements; the secondary valences are residual "affinities" which remain when the principal valences have been satisfied.

This theory of Werner, which started with the study of complex inorganic compounds of a very special nature, has gradually become of increasing importance as a theoretical basis of inorganic chemistry and the application of the theory is constantly being broadened. The electronic conception has helped to interpret the theory. Many compounds such as potassium ferrocyanide and ferricyanide, to which very complicated structural formulas were formerly assigned, are now much easier to understand. In the later chapters of this book this theory will be mentioned repeatedly.

103. Hydrofluosilicic Acid.

The reaction, $SiO_2 + 4\,HF = SiF_4 + 2\,H_2O$, is reversible. When warm and in the presence of sulphuric acid, which has a dehydrating action, it proceeds from left to right. If, however, silicon tetrafluoride is brought in contact with a large amount of water, then silicic acid and hydrofluoric acid are formed, but the hydrofluoric acid combines in a secondary reaction with undecomposed silicon fluoride to form hydrofluosilicic acid:

$$2\,HF + SiF_4 = H_2[SiF_6].$$

Place a mixture of 100 g. of powdered fluorspar and 40 g. of precipitated silicic acid, or 80 g. of sand, in a round-bottomed flask, and, while shaking, add 500 g. of concentrated sulphuric acid in small portions. Heat the mixture on a Babo funnel and conduct the escaping silicon fluoride into 1 liter of water by means of a dry delivery tube that dips directly into mercury which one-third fills a small beaker standing in the bottom of a large beaker containing the water. The lower end of the delivery tube should be made wider by sealing on a short piece of tube 1.5 cm. in diameter. The mercury keeps the opening of this tube dry and thus prevents it from becoming clogged with silicic acid. If the water becomes too much thickened with silicic acid, remove a part of the liquid without interrupting the process, filter it through a piece of linen laid in a large Büchner funnel, and return the filtrate to the beaker.

When the reaction is complete remove the silicic acid, as above, with a linen filter, and estimate the yield by analyzing a sample of the filtrate. Either titrate hot with 0.1-normal sodium hydroxide, using phenolphthalein as indicator, whereby the reaction is

$$H_2SiF_6 + 6\ NaOH = 6\ NaF + H_4SiO_4 + 2\ H_2O,$$

or else add to the solution an excess of neutral calcium chloride and titrate the hydrochloric acid set free, using methyl-orange as indicator:

$$H_2SiF_6 + 3\ CaCl_2 + 4\ H_2O = 3\ CaF_2 + 6\ HCl + H_4SiO_4.$$

Add some potassium chloride solution to another sample of the product; the difficultly soluble potassium salt separates, and, although the precipitate is barely visible at first, the liquid is eventually left in a jelly-like condition.

104. Potassium Titanium Fluoride, $K_2[TiF_6]$.

Allow 19 g. of titanium tetrachloride (No. 52) to flow very slowly from a dropping funnel into 20 c.c. of ice-cold water in a platinum dish. (Hood.) The dish must meanwhile be kept surrounded with ice. Add 30 g. of pure, 40 to 50% hydrofluoric acid to the mixture, and then a warm concentrated solution of 15 g. potassium chloride; the contents of the dish thereupon harden to a crystalline paste. Evaporate to complete dryness on the water bath, to remove the excess of hydrofluoric acid, and recrystallize the difficultly soluble residue from water. Yield, about 20 g.

105. Ammonium Plumbic Chloride, $(NH_4)_2[PbCl_6]$. Lead Tetrachloride, $PbCl_4$.

Triturate 10 g. of lead chloride, $PbCl_2$, with 20 c.c. of concentrated hydrochloric acid; after allowing the suspension to settle somewhat, decant off the solution together with the fine, suspended solid; repeat the above treatment with the residue until all of the lead chloride is in solution or in a state of finest suspension in 200 c.c. of hydrochloric acid.

Place mixtures prepared in this manner in each of two 250 to 300 c.c. gas-wash-bottles, and, while keeping the temperature at 10° to 15° and shaking occasionally, pass a slow current of chlorine through the two bottles placed in series. After about five hours all the lead chloride should be dissolved. If any remains, allow the solutions to stand overnight and then filter off any insoluble residue on asbestos. Combine the two filtrates in a 600 c.c. flask, cool the liquid with ice, and add an ice-cold solution of 8 g. ammonium chloride in 80 c.c. of water; after a short time a heavy, yellow, crystalline precipitate of ammonium plumbic chloride begins to separate. After several hours filter rapidly on a hardened filter, wash the precipitate with 50 c.c. of ice-cold alcohol and dry it at 50°. Yield, about 20 g.

On treating a sample of the ammonium plumbic chloride with water, it decomposes immediately, forming brownish-black hydrated lead dioxide which remains to some extent in colloidal solution.

Lead Tetrachloride. Mix 20 g. of ammonium plumbic chloride thoroughly, by means of a mechanically driven stirrer, with 60 c.c. of ice-cold, concentrated sulphuric acid. In a short time heavy, nearly colorless, oily drops of lead tetrachloride separate. By repeated decantation and stirring up with fresh portions of sulphuric acid, it is possible to separate all of the ammonium sulphate from the oil, and the latter then settles as a fairly clear layer. If the oil is allowed to remain long in contact with the sulphuric acid, lead sulphate is formed.

Lead tetrachloride decomposes with explosive violence when strongly heated.

106. Potassium Lead Iodide, $K[PbI_3] \cdot 2\ H_2O$.

Potassium lead iodide is stable only when in contact with a cold, concentrated solution of potassium iodide. If the solution is diluted with water, or even if it is merely heated, potassium iodide dissolves out of the solid compound, and lead iodide remains behind. On concentrating and cooling the solution, the double salt is again formed.

If a hot solution of 4 g. lead nitrate in 15 c.c. of water is mixed with a hot solution of 15 g. of potassium iodide in 15 c.c. of water, yellow lead iodide is at first precipitated. On cooling to room temperature, the crystals of lead iodide disappear and a very pale-yellow, felted mass of crystal needles is produced. On heating, the crystals of the double compound disappear with a re-formation of lead iodide; on cooling, the double salt is again produced. The change can be observed especially well if a drop of the hot solution is placed between a heated slide and cover glass under the microscope.

If it is desired to obtain the dry salt, it should be collected on a filter, and, without washing, pressed between filter papers and dried in a vacuum desiccator.

Potassium lead iodide possesses the remarkable property of being extremely soluble in acetone. If the preparation is treated while still moist with 10 to 15 c.c. of acetone, there is produced, even in the cold, a yellow solution from which the salt can be precipitated by addition of two or three volumes of ether. On evaporating the acetone solution, no well-formed crystals are obtained. If a few drops of this solution are allowed to evaporate on filter paper the salt is obtained in a state of very fine subdivision, in which condition it is extremely sensitive to the least traces of moisture. Even the moisture of the air suffices to decompose the salt in a short time; the yellow color of lead iodide which thereby appears indicates in the sharpest manner the presence of traces of water. If another paper prepared in the same manner is left in a vacuum desiccator over sulphuric acid, no noticeable yellow color appears; on opening the desiccator, however, it develops immediately.

107. Potassium Mercuric Iodide, $K_2[HgI_4] \cdot 2\,H_2O$.

Precipitate mercuric iodide from an aqueous solution of 13.5 g. mercuric chloride by adding a solution of 16.6 g. potassium iodide. Wash the precipitate and then redissolve it in a hot solution of 16 g. potassium iodide in 10 c.c. of water. Filter off the small amount of undissolved mercuric iodide and allow the double salt to crystallize in a vacuum desiccator over sulphuric acid, breaking up occasionally the crust which forms over the surface. When a thick, pasty mass of crystals is obtained, drain off the liquid with suction, and without washing dry the light-yellow, prismatic crystals in a desiccator. Obtain more of the product from the mother-liquor.

Test-Tube Experiments. 1. Treat a little mercuric oxide with a few cubic centimeters of potassium iodide solution. A colorless, strongly alkaline solution containing potassium mercuric iodide and potassium hydroxide is produced. The formation of the complex salt makes it possible for the mercuric oxide to dissolve with the liberation of free potassium hydroxide (cf. No. 112).

2. Heat a sample of the dry salt in a test-tube. In addition to a little water, mercuric iodide distils off and condenses in the yellow modification on the cooler part of the tube. After some time, or more quickly on touching it with a glass rod, the sublimate changes into the red form, and this can again be changed into the yellow condition by heating (cf. Prep. 17).

108. Potassium Cobalticyanide, $K_3[Co(CN)_6]$.

Triturate 30 g. of cobalt carbonate with a little water until it is thoroughly wet; then suspend it in 100 c.c. of water and dissolve it by adding a solution of 110 g. potassium cyanide in 400 c.c. of water. Oxidize the potassium cobaltocyanide thus formed by drawing a vigorous current of air through the liquid for an hour. After filtering the dark-yellow solution, add to it 40 g. of glacial acetic acid and evaporate it to crystallization under a well-ventilated hood outside of the general laboratory. Drain the crystals, and wash them with alcohol of about 66% by volume. Work up the mother-liquor repeatedly as long as a sample of the crystals obtained gives a deep-blue solution when heated with concentrated sulphuric acid. The easily soluble potassium acetate remains in the residual liquor. Recrystallize the combined fractions from a solution which is slightly acidified with acetic acid. Yield, about 60 g. The product may be used in No. 109.

109. Hydroferrocyanic Acid, $H_4[Fe(CN)_6]$.

Hydroferrocyanic acid can be obtained pure without difficulty, and differs in this respect from most of the related acids which are only stable in the form of their salts. Hydroferrocyanic acid is easily soluble in water and alcohol; but it can be readily precipitated as an addition product with ether, and the ether can be removed from the compound by heating it in a current of hydrogen at 80° to 90°.

Treat a solution containing 42 g. of potassium ferrocyanide (0.1 mol.) in 350 c.c. of water with 120 c.c. of concentrated hydrochloric acid; if any precipitate of potassium chloride separates, redissolve it by adding a little more water. Cool and add about 50 c.c. of ether. After standing for several hours, colorless, glistening, microscopic crystals separate which should be drawn off and washed with dilute hydrochloric acid containing a little ether. To remove any admixed potassium chloride, dissolve the product in 50 c.c. of alcohol, filter, precipitate again with 50 c.c. of ether, drain off the liquid, and wash the crystals with the ether. Bring the ether-hydroferrocyanic-acid compound into an Erlenmeyer flask, which is provided with an inlet and an outlet tube, and heat it in an atmosphere of dry hydrogen at 80° to 90° on the water bath. The ether is removed in this way in about an hour. Yield, about 12 g. The hydroferrocyanic acid is nearly colorless at first, but it quickly develops a light-blue color by contact with the air.

110. Cobaltous Salt of Hydromercurithiocyanic Acid, $Co[Hg(SCN)_4]$.

Prepare two solutions, one with 30 g. of mercuric chloride and 44.5 g. of potassium thiocyanate in 500 c.c. of water, and another with 20 g. of cobalt nitrate in 50 c.c. of water. Mix the two clear solutions; a shower of small, deep-blue crystals of the difficultly soluble double salt begins to fall at once. After standing 12 hours, drain the crystals, wash them with water, then with alcohol, and dry the product in the steam closet. The yield is nearly quantitative.

A sensitive test for mercury is based upon the formation of this salt; the test is so delicate that less than 0.01 mg. of mercury can be detected. Evaporate one small drop of dilute mercuric chloride solution on a microscope slide and moisten the residue, by means of a platinum wire, with a tiny droplet of cobaltous acetate dissolved in a concentrated aqueous solution of ammonium thiocyanate. Under the microscope, tiny, dark-blue needles will soon be seen; these often unite to form concentric aggregates. Rubbing with a platinum wire serves to start the crystallization.

Powdered cobaltous mercurithiocyanate in contact with concentrated sodium carbonate solution decomposes after a few hours: on filtering a residue of dull red cobaltous carbonate remains on the filter and the filtrate contains sodium mercurithiocyanate.

111. Potassium Cobaltothiocyanate, $K_2[Co(SCN)_4]$.

Prepare a hot, saturated solution of 14.5 g. of crystallized cobalt nitrate and 24 g. of potassium thiocyanate; let it cool, and after several hours remove the crystals of potassium nitrate which have separated and rinse them with 40 g. of amyl acetate, added in small portions, until they are nearly colorless. Add these washings to the main part of the liquid in a separatory funnel and shake thoroughly. Separate the two layers that form; this will require very close attention, since both are deep blue. Extract the aqueous layer once or twice more with 10 to 15 c.c. of amyl acetate. To obtain a good product it is necessary, before evaporating the amyl acetate solution, to free it mechanically from drops of aqueous solution by pouring it back and forth into clean, dry beakers. In order to crystallize the salt, evaporate off one-tenth of the amyl acetate under the hood, and to the cooled solution add slowly 50 to 60 c.c. of low-boiling ligroin. Drain off the crystals, wash them with ligroin, and dry them over sulphuric acid. The product consists of deep-blue needles; when dissolved in water, it dissociates and a red solution is formed; upon the addition of potassium thiocyanate the dissociation is driven back and the solution becomes blue. Instead of amyl acetate, ethyl acetate can be used in the above procedure.

By allowing a solution of this substance in amyl acetate to evaporate at room temperature, fairly large, dark blue, flat crystals can be obtained.

112. Cadmium Iodide, $Cd[CdI_4]$ (Autocomplex Compound).

Cadmium iodide is, according to Hittorf, the cadmium salt of the complex iodocadmic acid, $H_2[CdI_4]$. A compound of this nature, in which one and the same metal exercises different functions, is known as *auto-complex*. (W. Biltz, 1902.) In harmony with the complex nature of cadmium iodide, the simple ions Cd^{++} and I^- show a strong tendency to combine with each other, as is illustrated, for example, by the fact that when a solution of potassium iodide is treated with cadmium hydroxide, the liquid becomes strongly alkaline, due to the formation of undissociated cadmium iodide and potassium hydroxide.

Allow several rods of pure zinc to stand for about 24 hours in contact with a solution of 26 g. crystallized cadmium sulphate in 100 c.c. of water, until all the cadmium is precipitated as spongy metal. To test for complete precipitation treat a few drops of the solution with hydrogen sulphide; no cadmium sulphide should form. Purify the finely divided cadmium by boiling it repeatedly with water.

Boil the cadmium with 24 g. of iodine and 50 c.c. of water, in a flask with return condenser, until all the metal is dissolved (1 or 2 hours). Then continue the boiling in an open flask to remove any excess of iodine, filter, and concentrate the filtrate to crystallization. Work up the mother-liquor. Yield, 30 to 35 g. of nearly colorless, lustrous plates.

To show that the amount of cadmium ions in a concentrated cadmium iodide solution is very small, treat the last mother-liquor with hydrogen sulphide. A slight separation of cadmium sulphide takes place after some time, but the precipitation is incomplete.

NITRITO ACIDS AND THEIR SALTS.

113. Potassium Mercurinitrite, $K_3[Hg(NO_2)_5] \cdot H_2O$.

Treat 43 g. of yellow mercuric oxide in a 500 c.c. flask with 71 g. of potassium nitrite and 240 g. of 10% acetic acid, and shake frequently until all is dissolved. Filter and concentrate the solution to crystallization on the water bath. The separation of crystals is much aided by the cautious addition of some alcohol. Collect the crystals and work up the mother-liquor. Recrystallize the combined crude product from a little water to which a few drops of potassium nitrite solution have been added. Pale-yellow, lustrous prisms, or plates, are obtained which are easily soluble in water; by slow evaporation, crystal aggregates are sometimes obtained of finger length.

The small content of mercuric ions in the solution of this salt is shown by its indifference toward a solution of urea, or toward a cold sodium bicarbonate solution that is saturated with carbon dioxide; on the other hand, precipitates are produced by sodium carbonate and by sodium hydroxide. From this it follows that a potassium mercurinitrite solution contains mercuric ions in about the same concentration as a solution of mercuric chloride.

114. Sodium Cobaltinitrite; Potassium Cobaltinitrite.

Sodium Cobaltinitrite. Dissolve 50 g. of cobaltous nitrate and 150 g. of sodium nitrite in 150 c.c. of water. Cool the solution to 40° and, while shaking frequently, add 50 c.c. of 50% acetic acid, a little at a time. Then oxidize the cobaltous salt by drawing air through the liquid for half an hour (see No. 107). After some time filter off the precipitate, which consists of sodium cobaltinitrite and perhaps a little of the corresponding potassium salt. Stir this precipitate with 50 c.c. of water at 70°–80° and after 10 minutes filter off the solution. Combine the two filtrates, and by introducing 350 c.c. of 96% alcohol from the jet of the wash-bottle while stirring, throw down the sodium cobaltinitrite from the solution. After standing 2 hours collect the precipitate and wash it twice with 25 c.c. of alcohol. Yield, 51 to 52 g.

Purify the crude product by recrystallizing it in three portions, each of which is stirred up with 1.5 times its weight of cold water. Filter off the small undissolved residues, and precipitate each of the clear filtrates by injecting from the wash-bottle, as above, 50 c.c. of a mixture of alcohol and a little glacial acetic acid (70 : 1). Wash the precipitate with alcohol and ether, and dry it at a temperature not exceeding 80°. Yield, about 40 g.

Potassium Cobaltinitrite. To the combined mother-liquors from the above, add potassium chloride solution until precipitation is complete. Collect, wash, and dry the yellow, crystalline precipitate.

The aqueous solution of the readily soluble sodium cobaltinitrite is a useful reagent in testing for the presence of potassium ions.

115. Potassium Tetranitrito-diammine-cobaltate, $K[Co(NO_2)_4(NH_3)_2]$.

Dissolve 10 g. of cobaltous carbonate in a barely sufficient amount of hydrochloric acid, so that a trace of residue remains undissolved and the solution is only faintly acid. Dilute the solution to 200 c.c. with water and add 70 g. of ammonium chloride, whereupon the color changes from red to violet. Warm the liquid to 50° and add a solution of 100 g. of potassium nitrite in 100 c.c. of water which is likewise warmed to 50° (use a large beaker on account of foaming). Maintain the mixture at 50° for half an hour and then place it in the ice-chest for 24 hours. Dull-brown crystals and a fine yellow powder separate; the latter may be removed by rotating the mass two or three times with 100 c.c. of cold water and each time pouring the liquid and the suspended matter away from the brown crystals.

Dissolve the crude product in 150 c.c. of boiling water; filter and cool the filtrate at once, because the salt is decomposed in hot solution. The main part of the salt crystallizes on cooling; wash it with a little water and then with alcohol. The addition of alcohol and a little ether to the mother-liquor causes the remainder of the salt to precipitate, and this should be recrystallized from a little water. Yield, 8 g. of brown, lustrous crystals.

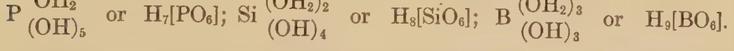
A cold saturated aqueous solution gives yellowish-brown prisms or rhombic leaflets when treated with mercurous nitrate solution.

HETEROPOLY ACIDS AND THEIR SALTS.

Among the compounds with complex anions belong a great number of complicated acids, many of them known only in the form of their salts, which are formed by condensation of oxy-acids. Such acids are often called *poly* acids; *heteropoly* acids if the condensed acids are unlike and *isopoly* acids if the condensation takes place from like constituents. The first classic representative of a heteropoly acid is phosphomolybdic acid (No. 116) which was discovered by Berzelius; almost equally well known is silicotungstic acid, discovered by Marignac. The components of condensed acids which come chiefly into consideration are, aside from those just mentioned, boric, stannic, arsenic and vanadic acids. To the group of isopoly acids belong the polychromic, polysilicic and polyboric acids. The study of such acids is complicated by the fact that the acids condense not only in one but often in several proportions. An acid of a particular composition, therefore, is produced only under certain definite conditions. Thus, a compound such as ammonium phosphomolybdate is well fitted for use in analytical chemistry for the precipitation of phosphoric acid, but it is only when the precipitate is produced under definite conditions that it is suitable as a form for weighing. There are, however, often clearly defined limits to the composition of the polyacids, since with a number of pairs no product can be obtained containing more than 12 molecules of the one acid anhydride to one molecule of the other.

The heteropoly acids crystallize exceptionally well. The crystals are often very soluble, sometimes even in organic solvents such as alcohols and ether. Drechsel has made use of their affinity for ether as a means for their purification. In the field of organic chemistry, certain of the heteropoly acids have been used as precipitants for high-molecular bases. Thus phosphomolybdic and phosphotungstic acids have been used for the detection of alkaloids and the latter can serve in the separation of the cleavage products of albumin. Further information concerning the preparation and analysis of polyacids may be found, for example, in a compilation by Rosenheim and Jaenicke, *Z. anorg. Chem.* **101**, 215 (1917).

The constitution of the polyacids is still a subject for speculation. Miolati and Rosenheim have assumed that one atom can be regarded as the central atom, around which six substituents are grouped. As the central constituent, phosphorus, silicon or boron can serve. Sometimes water, H_2O, serves as one of the six substituents and we have the following hypothetical acids:



$$P\genfrac{}{}{0pt}{}{OH_2}{(OH)_5} \text{ or } H_7[PO_6];\quad Si\genfrac{}{}{0pt}{}{(OH_2)_2}{(OH)_4} \text{ or } H_8[SiO_6];\quad B\genfrac{}{}{0pt}{}{(OH_2)_3}{(OH)_3} \text{ or } H_9[BO_6].$$

If to each of the 6 atoms of oxygen foreign acid anhydrides are added the following types of acids result:

$H_7P(W_2O_7)_6$	$H_8Si(W_2O_7)_3$	$H_9B(W_2O_7)_6$
phosphotungstic acid	silicotungstic acid	borotungstic acid

Pfeiffer has assumed an inner complex with a coördination number of 6 and an outer one with a coördination number of 12 and deduced a similar formula for phosphotungstic acid: — $H_7[(PO_6)(WO_3)_{12}]$.

Copaux assumes that two atoms of hydrogen can also act as the central atom. In this way the hypothetical acid $H_2\overset{(OH_2)_5}{\underset{O}{}}$ or $H_{10}(H_2O_6)$ is obtained, from which metatungstic acid, $H_{10}[H_2(W_2O_7)_6]$, is derived.

116. Ammonium Phosphomolybdate, $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot H_2O$.

Treat a concentrated solution of 24 g. ammonium molybdate with concentrated nitric acid until the precipitate of molybdic acid first appearing has redissolved and the solution remains clear even on boiling. On adding a solution of 3.6 g. of sodium phosphate the well-known, yellow precipitate is produced. Wash this and dry it in the steam closet. Yield, about 20 g.

117. Silicotungstic Acid, $H_8[Si(W_2O_7)_6] \cdot 29\,H_2O$.

First prepare silicic acid hydrogel by dissolving 50 g. of commercial, precipitated silicic acid in 12 g. of sodium hydroxide and 50 c.c. of water, diluting to 200 c.c., heating to about 100°, and precipitating with hydrochloric acid. Dilute further with hot water, drain the hydrogel on linen cloth in a large Büchner funnel and wash with hot water. Stir up the hydrogel in a dish with hot water and again drain it on the linen cloth.

Neutralize a solution of 50 g. pure, commercial sodium tungstate in 200 c.c. of water with about 80 c.c. of 2-normal sulphuric acid, using litmus paper as indicator. Have this solution boiling, add the hydrogel above obtained, and boil the mixture until a filtered sample no longer gives a yellow precipitate of tungstic acid when acidified with hydrochloric acid. During the boiling add a little 2-normal sulphuric acid whenever the solution becomes alkaline (in all about 20 c.c.). This operation should take half to three-quarters of an hour. Water should be added from time to time to replace that lost by evaporation. Finally, filter the solution.

Cool the filtrate, which amounts to about 200 c.c. in volume, and acidify it strongly by adding about 25 c.c. of concentrated sulphuric acid. Again cool and add ether, little by little with constant shaking, until on settling in a separatory funnel three layers are formed: on top an ethereal, in the middle an aqueous solution, and underneath a thick, oily layer of a liquid compound of silico-tungstic acid with ether. If this lowest layer does not form, or forms but incompletely, more sulphuric acid must be added. Allow the whole to stand over night, then draw off the bottom layer into a dry beaker, free it from drops of water by pouring it back and forth into dry beakers, and remove the ether by warming it for some time upon the water bath. Dissolve the residue in a little water, filter the solution, concentrate it to a small volume, and bring it to crystallization by surrounding the beaker with ice. If no crystals separate, the solution must be concentrated still further. Drain the crystals quickly from the liquid; do not wash this product, but free it from mother-liquor by spreading it on an unglazed plate. After the crystals have become white on the porous plate, dry them completely by letting them remain in a vacuum desiccator over sulphuric acid. Yield, 13 to 14 g.

When working with larger amounts of silicotungstic acid, large characteristic crystals can be obtained by slow evaporation in a vacuum desiccator.

ORGANOCOMPLEX COMPOUNDS.

118. Potassium Ferric Oxalate, $K_3[Fe(C_2O_4)_3]$; Platinotypes.

Oxidize a solution of 35 g. of crystallized ferrous sulphate in 100 c.c. of water by boiling it with just the necessary amount of nitric acid (test with potassium ferricyanide). Dilute the liquid to 2 liters, add ammonia and wash the precipitate of hydrated ferric oxide by decantation for several days, then collect it on a large, plaited filter and wash it with hot water.

To a hot solution of 44 g. of crystallized acid potassium oxalate in 100 c.c. of water add the ferric oxide hydrogel a little at a time until no more will dissolve. Such a solution is sensitive to direct sunlight. Filter and concentrate the filtrate to crystallization, wash the emerald-green crystals with water and alcohol, and dry them in a vacuum desiccator over sulphuric acid.

Platinotypes.

Potassium ferric oxalate is changed by the action of light to potassium ferrous oxalate, and the latter reduces platinum salts to metallic platinum.

Soak a piece of filter paper, the size of a photographic plate, with potassium ferric oxalate solution and dry it in the hot closet. Then place the paper in a shallow glass tray; wet it uniformly with about 2 c.c. of a 5% chloroplatinic acid solution, whereupon it turns yellowish red; and dry it again, avoiding any strong illumination. Then expose it for about an hour to a medium light under a paper stencil in a printing frame. At the end of the exposure, only the outlines of the pattern are to be distinguished, but the print may be developed by placing it for about one minute in a warm solution of potassium oxalate. Fix the "picture" in dilute hydrochloric acid, wash it repeatedly with water and then dry it. If potassium chloroplatinite is used instead of chloroplatinic acid the picture is developed of itself during the printing, but it should be fixed as in the preceding case by washing with dilute hydrochloric acid and water.

119. Optical Rotation of Uranyl Lævo-malate.

Aqueous, not too concentrated, solutions of ordinary malic acid rotate the plane of polarized light feebly toward the left. The presence of uranyl salts increases the extent of the rotation very considerably, and this is presumably due to the formation of complex compounds, although such substances have not yet been isolated. For this experiment a sensitive polarizing apparatus with graduations is necessary.

Prepare the following solutions: (I) 1.3 g. of malic acid in 10 c.c. of water; (II) 4 g. of uranyl nitrate in 10 c.c. of water; (III) 2 g. of potassium hydroxide in 20 c.c. of water.

First mix 1 c.c. of (I) and 2 c.c. of (III) and dilute to 20 c.c. Next prepare the same mixture of solutions (I) and (III), add 1.5 c.c. of solution (II) and dilute to 20 c.c. Determine in both samples the degree of rotation. If the polariscope is not very sensitive, use instead of the first mixture one which contains 5 c.c. of solution (I).

If c is the concentration of the malic acid, l the length of the tube (usually 20 cm.), and α_D the angle of rotation read with sodium light, then the specific rotation is $[\alpha]_D = \frac{100 \cdot \alpha_D}{c \cdot l}$. The experiment with malic acid gives for the value of $[\alpha_D]$ about $-3°$, with uranyl-malic acid, about $-475°$.

CHAPTER V.

COMPOUNDS CONTAINING A COMPLEX POSITIVE COMPONENT.

THE fundamental principles involved in the formation and dissociation of compounds containing complex cations are essentially the same as in compounds with complex anions. For example, hexamminenickelous bromide is formed as represented by the equation:

$$NiBr_2 + 6\,NH_3 = [Ni(NH_3)_6]\,Br_2;$$

hexaaquochromic chloride:

$$CrCl_3 + 6\,H_2O = [Cr(H_2O)_6]\,Cl_3;$$

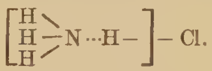
ammonium chloride is formed either in a similar manner:

$$NH_3 + HCl = [NH_3.H]\,Cl;$$

or by the association of the ions:

$$NH_4^+ + Cl^- = NH_4Cl.$$

The last two equations, viewed in the light of Werner's theory of secondary valences (cf. page 141), lead to the following structural formula:



$$\left[\begin{matrix} H \\ H \\ H \end{matrix}\!\!>\!N \cdots H-\right]-Cl.$$

Compounds with complex cations dissociate according to reactions which are the reverse of the reactions of their formation; naturally both formation and dissociation may take place in stages.

In the production of complex cations, ammonia and water come most frequently into consideration. Among the ammonia compounds, those in which ammonia, or a substituted ammonia, is joined to hydrogen (ammonium or substituted ammonium compounds) are to be distinguished from those in which ammonia, or a substituted ammonia, is joined to metal. The classification which follows is based upon this distinction.

Other complex-producing substances than those mentioned are less often met with. As representative of the compounds which they form, the nitric-oxide-metal compounds (cf. the well-known test for nitric acid with ferrous sulphate) may be mentioned, as well as the addition products with alcohol, ether, and ethyl acetate, which are similar in nature to the hydrates.

AMMONIUM COMPOUNDS AND SUBSTITUTED AMMONIUM COMPOUNDS.

120. Dissociation of Ammonium Chloride.

The fact that the vapor density determination of ammonium chloride shows the molecular weight to be but one-half the formula weight, leads to the conclusion that the number of molecules is doubled by the dissociation of the substance into ammonia and hydrogen chloride. If the compound is volatilized into an atmosphere either of ammonia or of hydrogen chloride, the dissociation is driven back in accordance with the mass-action law — this phenomenon being especially pronounced when working at lower temperatures and under reduced pressure. In the complete absence of water the dissociation fails to take place, thus showing in a remarkable manner the catalytic effect of traces of moisture.

The dissociation of ammonium chloride may be demonstrated qualitatively, by taking advantage of the greater velocity at which the lighter ammonia diffuses as compared with the heavier hydrogen chloride; the products of diffusion may be most conveniently separated by the use of a diaphragm.

Fasten a piece of combustion tubing, 20 cm. long, in a horizontal position. Insert a loose plug of asbestos at the middle of the tube, and place about a gram of ammonium chloride on one side of the plug. Heat the asbestos diaphragm and the ammonium chloride by means of a wide burner so that a slow sublimation takes place and the entire tube becomes filled with the vapors. After a few minutes test the gases at both ends of the tube with moist litmus paper. An acid reaction is shown on the side of the asbestos plug on which the solid salt was placed, while on the other side an alkaline reaction is obtained.

121. Hydroxylamine Sulphate, $[NH_2OH.H]_2SO_4$.

Sodium nitrite and sodium bisulphite react together in cold aqueous solution, at first molecule for molecule, forming *nitrososulphonate of sodium:*

$$\mathrm{ON}\boxed{\mathrm{ONa + H}}\mathrm{SO_3Na = NaOH + ON \cdot SO_3Na.}$$

Then, by the immediate taking up of a second molecule of sodium bisulphite, the stable sodium salt of *hydroxylaminedisulphonic acid* results:

$$\mathrm{ON \cdot SO_3Na + NaHSO_3 = HO \cdot N(SO_3Na)_2.}$$

If the solution is warm a third molecule of sodium bisulphite reacts and *nitrilo-sulphonate of sodium* is formed.

When heated above 100° with water the sodium salt of hydroxylaminedisulphonic acid is hydrolyzed into hydroxylamine and sodium bisulphate:

$$\mathrm{HO \cdot N(SO_3Na)_2 + 2\,H_2O = HONH_2 + 2\,NaHSO_4,}$$

and these substances interact to form hydroxylamine sulphate, $[HONH_3]_2SO_4$, and neutral sodium sulphate. The presence of barium chloride favors this reaction, since the sulphate ions are thereby precipitated as fast as they are formed. The filtrate then contains, in addition to free hydrochloric acid only hydroxylamine hydrochloride, $HONH_2 \cdot HCl$, and sodium chloride, and these can be separated by means of alcohol.

Hydroxylamine is of great importance in organic chemistry, where it is used both as a reducing agent and as a reagent for the carbonyl groups of aldehydes and ketones:

$$\underset{\text{acetone}}{(CH_3)_2C\boxed{O + H_2}}NOH = \underset{\text{acetone-oxime}}{(CH_3)_2C:NOH} + H_2O.$$

Hydrazine (No. 122) and semicarbazid (No. 123) show a similar behavior:

$$(CH_3)_2CO + \underset{\text{hydrazine}}{H_2N \cdot NH_2} = \underset{\text{acetone-hydrazone}}{(CH_3)_2C:N \cdot NH_2} + H_2O$$

$$2\,(CH_3)_2CO + H_2N \cdot NH_2 = \underset{\text{acetone-azine}}{(CH_3)_2C:N \cdot N:C(CH_3)_2} + 2\,H_2O$$

$$(CH_3)_2CO + \underset{\text{semicarbazide}}{H_2N \cdot NH \cdot CO \cdot NH_2} = \underset{\text{acetone-semicarbazone}}{(CH_3)_2C:N \cdot NH \cdot CONH_2} + H_2O$$

Saturate a solution of 143 g. crystallized sodium carbonate in 100 c.c. water with sulphur dioxide (from 150 g. copper and 600 g. concentrated sulphuric acid). Cool the solution to 0° with ice and salt, add 300 g. pulverized ice and then with mechanical stirring allow a solution of 60 g. of sodium nitrite in 100 c.c. water to drop in slowly. Finally add 50 c.c. of glacial acetic acid.

Place the solution in a round-bottomed flask, and heat it to boiling upon a Babo funnel. To the boiling liquid add a hot solution of barium chloride (about 250 g. of the crystallized salt in 300 c.c. water), avoiding an appreciable excess, until a little of the solution on being filtered is found free from sulphate. The duration of this operation is about one hour. Allow the liquid to settle, filter and evaporate the filtrate, at first over a free flame and finally to dryness on the water bath. Break up frequently the crusts of salt which are formed, and draw them up on to the sides of the dish. Place the anhydrous residue in a flask and extract it three times by boiling it with alcohol, using 200, 100, and 50 grams respectively of the latter; evaporate the alcoholic filtrate to a small volume, allow the solution to cool completely, collect the crystals on a filter, and evaporate the cold mother-liquor to obtain more crystals. Recrystallize the crude product from half its weight of hot water. Yield, 10 to 14 g. of hydroxylamine chloride.

Heat a trace of the hydroxylamine salt with Fehling's solution; cuprous oxide is precipitated.

Potassium Salt of Hydroxylaminedisulphonic Acid. On adding a saturated potassium acetate solution to some of the solution of the sodium salt of hydroxylaminedisulphonic acid obtained in the course of the foregoing procedure, crystals of the potassium salt $HO \cdot N : (SO_3K)_2$ are deposited. With potassium chloride the crystals separate more slowly.

Acetoneoxime, $(CH_3)_2C:NOH$. Add a solution of 8 g. sodium hydroxide in 12 c.c. water slowly and with constant stirring, but without cooling, to a mixture of 14 g. hydroxylamine hydrochloride, 12 g. acetone and 13 c.c. water. Acetoneoxime separates out as an upper layer which solidifies after standing for some time. After several hours pour off the aqueous solution and dissolve the oxime in ether, in which it is extremely soluble. Pass this solution through a dry filter to remove any suspended drops of aqueous solution, and evaporate the ether on the water bath, taking the usual precautions. On cooling, the oxime solidifies in beautiful crystals; if desired, it may be recrystallized from a low boiling ligroin. Yield, 10 to 13 g. Melting-point 59°–60°.

122. Hydrazine Sulphate, $[N_2H_4.H_2]SO_4$; Monochloramine, NH_2Cl.

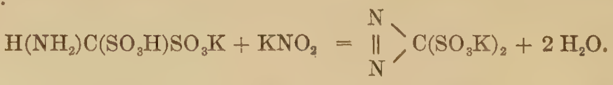
Hydrocyanic acid, as formed by the hydrolysis of potassium cyanide, unites in aqueous solution with two molecules of potassium bisulphite, forming *aminomethanedisulphonate of potassium:*

$$HCN + 2\,HSO_3K = H(NH_2)C(SO_3K)_2.$$

By strongly acidifying the solution with hydrochloric acid, the difficultly-soluble acid salt is precipitated:

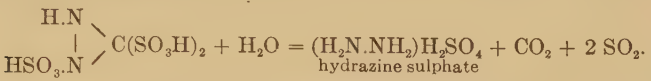
$$H(NH_2)C(SO_3H)SO_3K.$$

By "diazotizing" the amido group, *diazomethanedisulphonate of potassium* is obtained:



$$H(NH_2)C(SO_3H)SO_3K + KNO_2 = \begin{matrix} N \diagdown \\ \| \quad \\ N \diagup \end{matrix} C(SO_3K)_2 + 2\,H_2O.$$

This salt is capable of adding on one molecule of potassium sulphite at the point of the nitrogen double bond, and the acid corresponding to the salt thus formed breaks down with water, essentially into sulphur dioxide, carbon dioxide, and hydrazine sulphate:



$$\left.\begin{array}{r}\text{H.N}\\ |\\ \text{HSO}_3\text{.N}\end{array}\right\rangle C(SO_3H)_2 + H_2O = \underset{\text{hydrazine sulphate}}{(H_2N.NH_2)H_2SO_4} + CO_2 + 2\ SO_2.$$

Saturate a solution of 75 g. potassium hydroxide in 300 c.c. of water with sulphur dioxide. To the solution of potassium bisulphite thus prepared add 50 g. of powdered potassium cyanide (98–99%) while shaking; the yellow color of the bisulphite solution disappears, and the mixture becomes somewhat heated. After all the cyanide has dissolved, heat the solution on the water bath, and when, after some time, the liquid has become alkaline, acidify it cautiously with hydrochloric acid. Repeat the cautious additions of hydrochloric acid until the solution has become permanently acid. This operation requires from 1.5 to 2 hours, and in all about 30 c.c. of concentrated hydrochloric acid are necessary. Finally, add an additional 150 c.c. of concentrated hydrochloric acid and allow the mixture to stand in the ice-chest, when 60 to 80 g. of the crystals of acid potassium aminomethanedisulphonate are obtained. Collect this product on a filter and wash it with water.

Treat this salt in separate portions of 23 g. each as follows: stir each portion to a paste with 34 c.c. of water and then add to it a solution of 10 g. potassium nitrite in 6 c.c. water. The temperature of the mixture rises slowly to 40°–50° and within 10 or 15 minutes all of the solid salt has passed into solution. Make the solution alkaline with a little caustic potash and allow it to cool; about 18 g. of potassium diazomethanedisulphonate are deposited from each portion in the form of orange-yellow needles.

Dissolve the latter salt in a solution of an equal weight of crystallized sodium sulphite in two-thirds as much water; make the solution alkaline by the addition of a little sodium carbonate solution and then warm slightly until the color has disappeared. Finally, decompose the salt of the trisulphonic acid by adding an amount of 20% sulphuric acid equal to five times the weight of the salt. When the liquid no longer smells of sulphur dioxide, filter it and allow it to cool, whereby the hydrazine sulphate crystallizes out. Obtain a further yield from the mother-liquor and recrystallize the entire crude product from water. Yield, about 40% of the weight of the potassium diazomethanedisulphonate. Dependent preparation: Sodium Hydrazoate, No. 72.

Monochloramine, NH_2Cl; Hydrazine Sulphate according to Raschig.[1]

Ammonia is chlorinated by the action of sodium hypochlorite in dilute aqueous solution:

$$NH_3 + NaOCl = NH_2Cl + NaOH.$$

The monochloramine thus formed reacts with more ammonia to form hydrazine chloride:

$$NH_2Cl + NH_3 = H_2N . NH_2 . HCl.$$

Place 600 g. of ice and a cold solution of 85 g. of sodium hydroxide in 160 c.c. of water in a one-liter flask, weigh the flask and contents, wrap the flask in a towel, and pass in a rapid current of chlorine until the gain in weight is exactly 71 grams; avoid an excess of chlorine. Then on diluting to one liter, an approximately molal solution of sodium hypochlorite is obtained.

Monochloramine. Add 50 c.c. of this sodium hypochlorite solution to a mixture of 25 c.c. 2-normal ammonia and 75 c.c. of water. The liquid ceases to smell of ammonia, and in its place a peculiar, penetrating odor of monochloramine is noticeable which is similar to that of nitrogen chloride. Nitrogen is evolved from the solution at the same time, owing to the fact that monochloramine decomposes slowly in an aqueous solution according to the following equation:

$$3\ NH_2Cl = N_2 + NH_4Cl + 2\ HCl.$$

Hydrazine Sulphate. Mix 200 c.c. of 20% ammonia, 5 c.c. of a 1% gelatin solution, and 100 c.c. of the above prepared molal sodium hypochlorite in a one-liter Erlenmeyer flask, heat the mixture immediately to boiling, and boil it for half an hour. The solution is thereby concentrated to about one-fourth its original volume. Cool it, then add 25 c.c. of 2-normal sulphuric acid, and surround the flask with ice. Hydrazine sulphate crystallizes out in the form of glistening, transparent crystals which are obtained pure by recrystallizing from water. Yield, 5 to 6 grams.

This process, which is very interesting from a theoretical standpoint, is now used technically for the production of hydrazine sulphate, whereby the cost of the latter has been considerably reduced.

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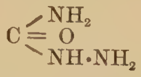
[1] Raschig, Ber. **40**, 4586 (1907).

123. Semicarbazide Hydrochloride.

From ammonia and cyanic acid urea can be obtained, with the intermediate formation of ammonium cyanate. From hydrazine, which is an amino substituted ammonia, semicarbazide



$$C{=}O\begin{cases}NH_2\\NH{\cdot}NH_2\end{cases}$$

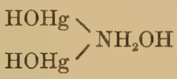
an analogous substituted urea is obtained. Semicarbazide, like free hydrazine, condenses with carbonyl groups (cf. Introduction to No. 121), and the semicarbazones thus formed being difficultly soluble, serve for the detection and isolation of carbonyl-containing compounds.

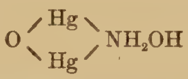
Dissolve 130 g. hydrazine sulphate and 54 g. anhydrous sodium carbonate in 50 c.c. of water, warm the solution to 50°–60°, and then add a solution of 86 g. potassium cyanate in 500 c.c. water. The next day filter off the few grams of secondary product which have separated, treat the filtrate with 120 g. of acetone and allow the mixture to stand in a flask, with frequent shaking, for another 24 hours. Drain the precipitated salt, and evaporate the mother-liquor to dryness on the water-bath, stirring towards the end. Place the entire amount of the salt in an automatic extraction apparatus, and extract it thoroughly with alcohol, in which the acetone-semicarbazone is more soluble than in acetone; a few cubic centimeters of acetone should be mixed with the alcohol. The acetone-semicarbazone crystallizes in the distilling flask of the extraction apparatus. After it is drained and washed with a little alcohol and ether, it melts at 186°–187°. Crystallize the remainder of the salt by evaporating the alcoholic mother-liquor somewhat and adding a little ether. Yield, 80%.

The above product can be transformed quantitatively into semicarbazide hydrochloride, as follows: Warm the acetone-semicarbazone gently with concentrated hydrochloric acid in the proportion of 11.5 g. of the former to 10 g. of the latter until the solid is just dissolved. On cooling, the solution solidifies to a thick paste of colorless, well-formed needles. Drain the product with suction and wash it with a little alcohol and ether; it melts at 173° with decomposition. To the mother-liquor, add double its volume of alcohol, and bring the rest of the salt to crystallization by adding ether.

124. Millon's Base.

Millon's base, $Hg_2NOH . 2 H_2O$, is formed by the action of mercuric oxide upon an ammonia solution. Since, by merely heating, this compound is changed first to the monohydrate and then to dimercuriammonium hydroxide, Hg_2NOH, it follows that in Millon's base itself the mercury is probably united to the nitrogen atom, as is unquestionably the case in the dehydration product. Whether the water is present in the compound as water of crystallization, or whether it is combined by atomic valences, has not been established. In the latter case Millon's base would be regarded as dihydroxydimercuriammonium hydroxide (I) and its first dehydration product as oxydimercuriammonium hydroxide (II);


(I)


(II).

The ability of mercury to replace hydrogen in certain compounds, with the formation of substances like the above, which are stable in presence of water, is also apparent in several series of mercury organic compounds.

Treat a solution of 25 g. mercuric chloride in 200 c.c. of water at 70° with a solution of 7.5 g. sodium hydroxide in 20 c.c. water, wash the resulting precipitate several times by decantation, collect it on a suction filter and wash it further with water. Meanwhile prepare a carbonate-free solution of ammonia by distilling a mixture of 150 g. concentrated ammonia with 20 g. of lime, first placing 100 c.c. of cold water in the receiver. Introduce the moist mercuric oxide into this ammonia solution and allow the mixture to stand with frequent shaking for a day or two in the dark. Collect the product on a suction filter, wash it with water, alcohol and finally with ether, and dry it at the temperature of the laboratory.

Salts of Millon's Base.

When solutions of ordinary salts are treated with Millon's base, salts of the latter, which are very difficultly soluble, and free metal hydroxide, are formed.

Shake a little of Millon's base with a dilute solution of potassium iodide. The solution becomes alkaline, and the brown residue is, in all probability, identical with the well-known precipitate obtained in the test for ammonia with Nessler's reagent. Filter the solution through a double filter of hardened paper, and clarify the turbid filtrate by shaking it with pieces of torn filter paper and again filtering. The solution, after being acidified with nitric acid, gives no precipitate with silver nitrate.

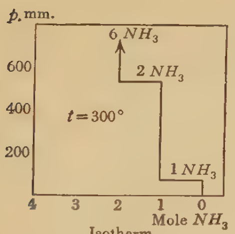
A dilute solution of copper sulphate, or one containing ferric chloride, when shaken with Millon's base, is entirely freed from all dissolved salt.

Oxydimercuriammonium hydroxide. Spread 10 g. of Millon's base in a thin layer on a watch-glass and allow it to dry for five days over lime in a desiccator, adding in the first place 0.5 to 1 c.c. of concentrated ammonia to the lime so that an atmosphere of ammonia is produced. The product is explosive. Clamp a test-tube containing a *small* amount of the substance in an upright position and heat it behind the lowered window of the hood.

METAL-AMMONIA COMPOUNDS.

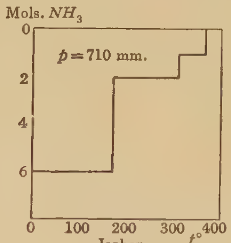
The importance of the metal-ammonia compounds lies in their great number,[1] in their stability, and in the significance of the theoretical questions pertaining to them. Among the best known of these compounds are those containing tervalent cobalt, chromium, rhodium and iridium. Metal-ammonia compounds are formed by the addition of gaseous ammonia to the solid salts, or by the union of the two components in solution.

The first method, inasmuch as it represents the combination of two substances of widely different volatility (very difficultly volatile metal salt and gaseous ammonia), offers opportunity for the investigation of these substances from the standpoint of heterogeneous equilibrium.



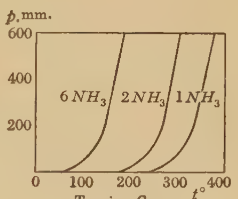
Isotherm

FIG. 22a



Isobar

FIG. 22b



Tension Curves

FIG. 22c

Of the three variables, pressure, p, temperature, t, and concentration, c, which determine the condition of a system, one may hold any one constant and follow the variation of the other two with respect to each other. With temperature constant, the curve obtained by plotting concentration against pressure is known as an *isotherm.* With pressure constant the plot of concentration against temperature is an *isobar;* each compound has a definite limit (similar to a boiling point) beyond which it changes abruptly into the next lower compound of the series. When pressure and temperature are both variable, a curve appears for each compound quite of the nature of a vapor pressure curve which is known as a *tension curve.* Along this curve the particular compound can exist in equilibrium with the vapor and the next compound of the series. In the area between two curves only the one compound can exist in equilibrium with the vapor.

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[1] Werner estimates the number of compounds of the general formula $MX_n(NH_3)_m$ as 1700.

By studying isobars and isotherms it is possible to determine the number and composition of all compounds of gaseous ammonia and a given salt and to characterize the individual compounds by the tension curves which separate the fields of their existence. The decomposition temperature, T on the absolute scale, is, for different compounds at the same pressure, proportional to the mutual affinities of the salt and ammonia. These studies show, therefore, not only what particular ammoniates can exist but they give us a rational means of measuring the affinities of salts toward ammonia. Fig. 22*a* is the isotherm curve for the system $NiCl_2/NH_3$. The curve shows that $NiCl_2$ forms a monammine which has a pressure of 74 mm. at 300°, a diammine with a pressure of 540 mm. and a hexammine with a pressure of more than an atmosphere. If the pressure is kept constant at 710 mm., Fig. 21*b*, shows that the hexammine is stable up to 176°, the diammine up to 311° and the monammine to 375°. Fig. 21*c* shows, by tension curves, the separate fields in which the three ammoniates can exist.

The second method of preparing complex metal-ammonia compounds, i.e. by the combination of metal salt and ammonia in aqueous solution, has been up to the present time the one most used. It should be noted, however, that the principal form in which the complex salt exists in the solution is not necessarily that form in which it crystallizes out. The determination of the stoichiometric composition of dissolved metal-ammonia salts in the presence of an excess of ammonia is possible by a combination of different physico-chemical methods (solubility measurements, and determinations of ion concentrations by measuring the electromotive force). Thus it has been found that the composition of the silver-ammonia ion which preponderates in aqueous solution is $[Ag(NH_3)_2]^+$, whereas the salt separating from such a solution has the formula $2\ AgCl \cdot 3\ NH_3$.

The question, with which of the components of the salt is the ammonia combined, can be answered by the physico-chemical behavior of the compound (conductivity and transference number) and also in a purely chemical way. A solution of a cupric salt to which an excess of ammonia is added possesses a deep-blue color instead of the usual light-blue of copper ions, and the addition of sodium hydroxide solution no longer causes a precipitation of cupric hydroxide. From this, and from the fact that electrolysis of the solution causes copper to migrate as before towards the negative pole, the conclusion is drawn that the copper ions have disappeared and been replaced by new cations containing copper, and that these can have been formed only by the adding of ammonia to the copper. The investigation of other metal-ammonia salts has led to corresponding results: ammonia is usually found in the cation.[1]

Whether other components than ammonia take part in the formation of the complex ions is ascertained, first by conductivity measurements, from which the number of ions contained in the solution is determined, and second by chemical reactions from which the composition of the ions can be deduced. If the molecular conductivity, α, of 1/512 normal or 1/500 normal solutions at 25° is compared as follows:[2]

	$Co(NH_3)_6X_3$	$Co(NH_3)_5X_3$	$Co(NH_3)_4X_3$	$Co(NH_3)_3X_3$
α	402	245	117	7

and at the same time the conductivity of the following types of simple salts under the same conditions:

	Na_3PO_4	$MgCl_2$	$NaCl$
α	370	249	125

is taken into consideration, it follows that the first of the above complex salts must be a quaternary electrolyte, the second a ternary one, the third a binary one, while the fourth is not an electrolyte at all; this is expressed by the following formulas:

$$[Co(NH_3)_6]X_3 \qquad [Co(NH_3)_5X]X_2 \qquad [Co(NH_3)_4X_2]X \qquad [Co(NH_3)_3X_3]$$

A confirmation of this view is furnished by the chemical reactions of the compounds. If, for example, X is a halogen, then in a solution of the compound $[Co(NH_3)_5Br]Br_2$ only two-thirds of the bromine is precipitated by the addition of silver nitrate. In a similar way it has been found, in numerous cases, that the deductions from conductivity measurements are in accord with the chemical behavior of substances, and thus it is shown that in addition to ammonia, also certain atoms and radicals which usually act as anions (e.g. the halogens, NO_2, and CO_3) may participate in the formation of complex cations.

In one series of metal-ammonia salts the compounds as they exist in the solid state contain water which cannot be removed without destroying the compounds. This water remains as a constituent of the salts even when their negative components are replaced by others, and it must therefore belong to the cation (cf. No. 134)

$$[Co(NH_3)_5H_2O]Cl_3 + 3AgNO_3 = [Co(NH_3)_5H_2O](NO_3)_3 + 3\ AgCl.$$

The water apparently plays the same part in these compounds as ammonia in the first-mentioned series, as is evident from the fact that the conductivity is not materially changed when molecules of ammonia in one of the above compounds are replaced successively by water molecules:

	$[Co(NH_3)_6]Br_3$	$[Co(NH_3)_5H_2O]Br_3$	$[Co(NH_3)_4(H_2O)_2]Br_3$
α	402	390	380

---

[1] For exceptions to this general rule see No. 115 and p. 169 (top).

[2] These values are taken from measurements on $[Co(NH_3)_6]Br_3$, $[Co(NH_3)_5Br]Br_2$, $[Co(NH_3)_4Cl_2]Br$, and $[Co(NH_3)_3(NO_2)_3]$ Werner and Miolati; Z. phys. Chem. **12**, 35 (1893); **14**, 506 (1894); **21**, 225 (1896).

Besides ammonia a number of other substances of similar nature, such as ethylene diamine and pyridine, often take part in the formation of complex cations.

A comparison of the composition of a large number of complex compounds which have been carefully studied from different points of view has shown that here, as in the case of the complex anions, the number of atoms or atomic groups which are attached to a single metal atom is in a majority of cases either four or six. Werner[1] accounts for this by assuming here also that the constituents forming the complex are situated around the central metal atom either in the four corners of a square or in the six corners of an octahedron. The ever-recurring coördination numbers 4 and 6 would thus be a measure of the available space around the central atom, but they are quite independent of the valence of this atom. This space, which Werner designates as the "inner sphere" is characterized by the fact that no components can be dislodged from it by electrolytic dissociation and that the whole is able to take part in chemical reactions exactly in the same way as an individual metal atom. The valence of the complex is equal to the difference between that of the central atom and the valence of the attached acid radicals. If the valences of the acid residues are sufficient to satisfy that of the central atom, then the total valence of the complex is zero, i.e. the substance is a non-electrolyte, e.g. trinitrito-triammine-cobalt. (No. 139.)

Nomenclature. Before the constitution of the metal-ammonia compounds was known certain series were designated according to their external characteristics (e.g. color, in roseo salts and purpureo salts) while others were named after the discoverer (e.g. Magnus' salt). Werner, after formulating his theory, proposed a rational system of nomenclature which is now quite generally adopted. According to this system the names of the constituents belonging to the complex cation are placed before the name of the metal and are arranged in the following order: first the acid radicals; then any groups which behave in the same manner as ammonia; and lastly, just preceding the metal, the ammonia itself. The acid radicals are given the suffix "*o*" while ammonia is designated by the term "*ammine,*" and water contained in the complex is designated as *aquo*. The number of each kind of constituent is indicated by the appropriate prefix, *di*, *tri*, etc. The complete name of the cation is commonly printed as a single word. The anions are designated in the usual way and follow the name of the cation. Further particulars will be evident from a study of the examples in the accompanying tables, pp. 167 and 168.

Isomerism. It is apparent from the tables on the following two pages that in certain cases two compounds exist which have the same empirical composition, and the same molecular weight, but still have different properties (isomerism). The existence of such isomers leads here, as in all similar cases, to the assumption that there is a definite spatial arrangement of the various parts of the molecule and gives justification for the arbitrary assump-

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[1] Neuere Anschauungen auf dem Gebiete der anorganischen Chemie, 4th Ed. Braunschweig 1919.

TABLE I. — COBALTIAMMONIA COMPOUNDS.

Rational Name.	Formula.	Old Name.
	1. *With Trivalent Cation.*	
Hexamminecobaltic Salts	$[Co(NH_3)_6]X_3$	Luteocobaltic Salts (No. 133).
Aquopentamminecobaltic Salts	$[Co(NH_3)_5H_2O]X_3$	Roseocobaltic Salts (No. 134).
Diaquotetramminecobaltic Salts	$[Co(NH_3)_4(H_2O)_2]X_3$	Tetrammineroseocobaltic Salts (No. 136).
	2. *With Bivalent Cation.*	
Chloropentamminecobaltic Salts	$[Co(NH_3)_5Cl]X_2$	Chloropurpureocobaltic Salts (Nos. 130–132, 135).
Nitritopentamminecobaltic Salts[1]	$[Co(NH_3)_5NO_2]X_2$	Xanthocobaltic Salts.
Chloroaquotetramminecobaltic Salts	$[Co(NH_3)_4H_2O.Cl]X_2$	Chloropurpureotetramminecobaltic Salts (Nos. 130, 138).
	3. *With Monovalent Cation*	
Dichlorotetramminecobaltic Salts	$[Co(NH_3)_4Cl_2]X$	Dichloropraseocobaltic Salts (No. 138).
Dibromotetramminecobaltic Salts	$[Co(NH_3)_4Br_2]X$	Dibromopraseocobaltic Salts (No. 135).
1.6 Dinitritotetramminecobaltic Salts[2]	$[Co(NH_3)_4(NO_2)_2]X$	Croceobaltic Salts.
1.2 Dinitritotetramminecobaltic Salts[2]		Flavocobaltic Salts (Nos. 136–138).
Carbonatotetramminecobaltic Salts	$[Co(NH_3)_4CO_3]X$	(No. 129).
	4. *Undissociated Compound.*	
Trinitritotriammine Cobalt	$[Co(NH_3)_3(NO_2)_3]$	Triamminecobaltic Nitrite of Gibbs or of Erdmann (No. 139).

---

[1] Recently Werner has designated the group NO_2 in the complex as *nitro* (1907).

[2] See Introductory part to No. 138.

TABLE 2. — PLATINOAMMONIA COMPOUNDS.[1]

Rational Name.	Formula.	Old Name.
Tetrammineplatinous Salts	$[Pt(NH_3)_4]X_2$	Platodiammine Salts: Salts of the *first* Reiset Base (Nos. 141 and 142.)
Chlorotriammineplatinous Salts	$[Pt(NH_3)_3Cl]X$	Platomonodiammine.
1.3 Dichlorodiammine Platinum	$[Pt(NH_3)_2Cl_2]$	Platosammine Chloride; Chloride of the *second* Reiset Base (No. 143).
1.2 Dichlorodiammine Platinum		Platosemidiammine Chloride; Salt of Peyrone (No. 143).

TABLE 3. — PLATINIAMMONIA COMPOUNDS.[1]

Rational Name.	Formula.	Old Name.
Hexammineplatinic Chloride	$[Pt(NH_3)_6]Cl_4$	Chloride of Drechsel's Base.
Dichlorotetrammineplatinic Salts	$[Pt(NH_3)_4Cl_2]X_2$	Platindiammine; Salt of Gros's Base.
Trichlorotriammineplatinic Salts	$[Pt(NH_3)_3Cl_3]X$	Platinmonodiammine Salts.
1.6 Tetrachlorodiammine Platinum	$[Pt(NH_3)_2Cl_4]$	Platiniammine Chloride; Gerhardt's Salt.
1.2 Tetrachlorodiammine Platinum		Platinisemidiammine Chloride.

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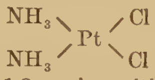
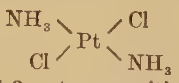
[1] The use of the discoverer's name is less customary in the more recent literature; but on the other hand, the old rational designations, which originated with Blomstrand, and are given in the same column in the above tables, are still often employed. This leads to confusion because according to the Blomstrand momenclature "ammine" usually signifies *two* ammonia molecules.

tion that the constutuents of the "inner sphere" which surrounds the central metal atom are actually situated at the corners of a square or of an octahedron. Two different pairs of substituents are manifestly capable of two different arrangements at the corners of a square:



1.2 or cis-position



1.3 or trans-position.

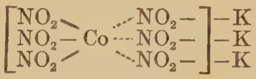
If, however, three substituents in a square are the same and the fourth different, such an isomerism is impossible. The actual lack of isomers in the latter case and their existence in the former, strongly support the above assumption.

Similarly, the isomerism of the two dinitritotetramminecobaltic series is explained by the use of the corresponding octahedral formulas (cf. No. 138).

As has already been stated, the external valence of the complex is equal to the difference between the valence of the metal and the total valence of the acid radicals contained in the complex. This external valence may become zero, or even negative when the valence of the acid part of the complex preponderates. In the following series of seven cobalt compounds, the valence of the complex changes progressively from three positive to three negative:

$[Co(NH_3)_6]Cl_3$ $[Co(NH_3)_5NO_2]Cl_2$ $[Co(NH_3)_4(NO_2)_2]Cl$ $[Co(NH_3)_3(NO_2)_3]$
$K[Co(NH_3)_2(NO_2)_4]$ (No. 115) $K_2[Co(NH_3)(NO_2)_5]$
$K_3[Co(NO_2)_6]$ (No. 114).

The binding power for potassium, or in other words the affinity for negative electrons, is occasioned by the valences of the nitrite radicals. The binding of these nitrite groups within the complex takes place in part by means of the secondary valences (cf. pp. 141 and 155).



so that of the six nitrite groups attached to the cobalt, three are held by the principal valences and three by the secondary valences of the metal. Inasmuch as the secondary valences are weaker than the principal ones, this view corresponds well with the formation of potassium cobaltinitrite from potassium nitrite and cobaltic nitrite, and with its manner of ionizing. For the further development of this theory, which leads to the conception of "indirect combination," the work of Werner already cited should be consulted.

125. Silver-ammonia Sulphate $[Ag(NH_3)_2]_2SO_4$.

Diamminesilver sulphate can be prepared in the solid form although this is not possible with the corresponding chloride (cf. p. 164).

Treat 10 g. of silver nitrate with 31 c.c. of 2-normal sulphuric acid and heat the mixture in a small evaporating dish on an air bath, until no more acid vapors are given off. While still hot dissolve the perfectly dry residue in the least amount possible of concentrated ammonia (Hood). Filter the solution and allow it to crystallize. Recrystallize the crude product from water containing a little ammonia. Yield, about 5 grams of colorless, columnar crystals.

Analyze the product by determining the silver as AgCl and the ammonia by distilling with caustic soda and titrating the distillate.

126. Tetramminecupric Sulphate, $[Cu(NH_3)_4]SO_4 \cdot H_2O$, and Ammonium Cupric Sulphate, $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$.

The first of these salts may be regarded as ordinary blue vitriol in which four molecules of water have been replaced by ammonia. The fifth molecule of water evidently has another function from that of the other four, cf. p. 191 (top).

Dissolve 20 g. of powdered blue vitriol in a mixture of 30 c.c. concentrated ammonia and 20 c.c. of water and precipitate the deep-blue solution (first filtering it through asbestos if necessary) by the gradual addition of 30 c.c. alcohol. After standing for some hours in the cold, filter off the dark-blue crystals with suction, and wash them first with a mixture of equal volumes of alcohol and concentrated ammonia and finally with alcohol and ether. Dry the salt at the laboratory temperature. Yield, almost quantitative.

Ammonium Cupric Sulphate crystallizes on cooling from a hot solution of 25 g. blue vitriol and 13.25 g. ammonium sulphate in 40 c.c. of water. Recover the last portions of the salt by concentrating the mother-liquor. The yield is nearly quantitative, and consists of large, light-blue crystals. The aqueous solution of the salt gives a precipitate of cupric hydroxide on being treated with sodium hydroxide. The salt belongs to the large class of monoclinic double salts which crystallize with six molecules of water.

127. Tetramminecupric Chloride, $[Cu(NH_3)_4]Cl_2 \cdot H_2O$.

In order to prepare this salt, which is readily soluble in water, conduct ammonia gas through a wide delivery tube into a warm filtered solution of 17 g. crystallized cupric chloride in 15 c.c. of water. The ammonia gas is obtained by heating 100 c.c. of concentrated ammonia solution gently and passing the gas through an empty wash-bottle to free it to some extent from water vapor.

The mixture becomes heated to boiling as a result of the reaction, and it should therefore be cooled somewhat to prevent too much evaporation. When a clear, deep-blue solution is obtained add 8 c.c. of alcohol and again saturate the liquid with ammonia, this time cooling it with ice. Drain the deposited salt on a hardened filter, wash it with alcohol to which a little concentrated ammonia has been added, then with pure alcohol and finally with ether, and suck it as dry as possible. Yield, 15 to 18 grams. The preparation must be placed immediately in a stoppered bottle, as it loses ammonia on standing in the open air. The addition of the alcoholic washings to the mother-liquor causes the precipitation of a few grams more of finely-divided and consequently lighter-colored product.

128. Hexamminenickelous Bromide, $[Ni(NH_3)_6]Br_2$.

Hexamminenickelous bromide can be used in making cobalt-free preparations of nickel such as are required for atomic weight determinations. The corresponding cobalt salt is far more soluble. The raw material used and the final product obtained should be tested qualitatively for cobalt.

Pour a solution of 141 g. crystallized nickel sulphate in 4 liters of water into a large flask and add a solution of 41 g. sodium hydroxide in 200 c.c. of water. Wash the resulting, voluminous, light-green precipitate by decantation; let it settle as much as possible, then siphon off the supernatant liquid and fill the flask again with distilled water; repeat this process from time to time for from three to five days. Collect the washed precipitate upon a large plaited filter and dissolve it in an aqueous solution of hydrobromic acid containing about 82 grams of the acid.[1] Evaporate the filtered solution to dryness on the water-bath, take up the residue in as little water as possible, cool the solution to 0° with a mixture of ice and salt and then treat it with concentrated ammonia; an abundant precipitate of violet, micro-crystalline flakes is obtained and the liquid becomes colorless. After standing for a short time at 0°, collect the crystalline mass on a suction-filter, wash it carefully with ice-cold ammonia (to remove any cobalt present), and dry it in a desiccator over lime which is mixed with a little solid ammonium chloride. The yield is almost theoretical. If desired the preparation can be carried out on a smaller scale.

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[1] Cf. No. 35.

129. Carbonatotetramminecobaltic Nitrate, $[Co(NH_3)_4CO_3]NO_3 \cdot \frac{1}{2}H_2O$.

When cobalt salts are treated out of contact with the air with an excess of ammonia, hexamminecobaltous salts are formed. If such a solution is mixed with a large amount of ammonium carbonate, oxidized by the air, and then evaporated to a small volume with the addition of more ammonium carbonate, crystals of carbonatotetramminecobaltic salt are produced.

Dissolve 20 g. of cobalt carbonate in as little concentrated nitric acid as possible and dilute the solution to 100 c.c. (or 50 g. of crystallized cobaltous nitrate may be dissolved in an equal amount of water).

Dissolve 100 g. of ammonium carbonate in 500 c.c. of water in a 1-liter flask, add 250 c.c. of concentrated ammonia, and into this solution pour the above prepared solution of cobalt nitrate. Draw a stream of air through the deep-violet-colored liquid in the manner described under No. 108. At the end of three hours, pour the liquid, which is now of a blood-red color, into a porcelain evaporating dish, and concentrate it to about 300 c.c., adding 5 g. of powdered ammonium carbonate every fifteen minutes (about 25 or 30 grams in all). Filter the solution immediately from any small amount of sediment and boil it down to 200 c.c., still continuing to add ammonium carbonate in small quantities (about 10 g. in all during this final evaporation). Allow the liquid to cool and collect the large, purple crystal-plates which separate out. Wash the crystals with a little water, then with dilute alcohol and finally with pure alcohol. Recover a crop of impure crystals by concentrating the mother-liquor; extract this product at the laboratory temperature with 15 times its weight of water, and precipitate the salt from the filtered solution by gradually adding two to three volumes of alcohol. Collect this precipitate and wash it as directed above. Total yield, 22 to 25 grams.

130. Chloropentamminecobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$, from the preceding.

The preparation of chloropentamminecobaltic chloride from the carbonatotetrammine salt is an example of the replacement of certain constituents in the complex by means of others. On acidifying an aqueous solution of the carbonatotetrammine salt with hydrochloric acid, there is formed, for the most part, chloroaquotetramminecobaltic chloride. This is changed, on being heated in an ammoniacal solution, into aquopentamminecobaltic chloride, and the latter on being acidified with hydrochloric acid is converted into chloropentamminecobaltic chloride. This is one of the best and longest-known members of the entire series, and has, on account of its color and chlorine content, been called chloropurpureocobaltic chloride. It may also be prepared by thermal decomposition of luteocobalt chloride.

Add concentrated hydrochloric acid (about 4.5 c.c.) to a solution of 3 g. carbonatotetramminecobaltic nitrate in 40 c.c. of water until all the carbon dioxide has been expelled. Then make the solution slightly ammoniacal; thereupon add an excess of 5 c.c. concentrated ammonia and heat the solution for three-quarters of an hour on the water-bath. After cooling add 50 c.c. of concentrated hydrochloric acid and heat the mixture once more for an hour on the water-bath. Drain the violet-red salt which separates and wash it with alcohol. Yield, 1.5 to 2.5 grams.

✓131. Chloropentamminecobaltic Chloride from Cobalt Carbonate.

By oxidizing a strongly ammoniacal solution of hexamminecobaltous chloride containing a large amount of ammoniumcarbonate, carbonatotetramminecobaltic chloride (cf. No. 129), aquopentamminecobaltic chloride, $[Co(NH_3)_5H_2O]Cl_3$, and oxycobaltammine chloride, $[Co_2O_2(NH_3)_{10}]Cl_4$, are formed. By adding ammonium chloride in considerable quantity to the solution and evaporating, the last-mentioned compound is converted into chloropentamminecobaltic chloride, or into aquopentamminecobaltic chloride. These substances, like carbonatotetramminecobaltic chloride, can be converted into chloropentamminecobaltic chloride (cf. preceding preparation).

Dissolve 20 g. of cobalt carbonate in as little hydrochloric acid as possible and treat the filtered solution in the cold with 250 c.c. of 10% ammonia and 50 g. of ammonium carbonate dissolved in 250 c.c. of water. Oxidize the mixture by passing through it a rapid current of air for three hours (cf. No. 107). Then add 150 g. of ammonium chloride and evaporate the solution on the water-bath until it becomes of pasty consistency. Acidify with hydrochloric acid, while stirring, until no more carbon dioxide is evolved and then make ammoniacal once more, adding 10 c.c. of concentrated ammonia in excess. After diluting to 400–500 c.c. heat the mixture again on the water-bath for an hour. Add 300 c.c. of concentrated hydrochloric acid and leave the solution on the water-bath until, at the end of from half to three-quarters of an hour, a separation of chloropentamminecobaltic chloride takes place. After cooling, filter off the crystals and wash them with dilute hydrochloric acid.

For purification, dissolve the crude product in 300 c.c. of two per cent ammonia solution, whereby aquopentamminecobaltic chloride is formed (cf. No. 134), extract the residue twice with 50 c.c. of the same ammonia solution, and precipitate the filtrate by adding 300 c.c. of concentrated hydrochloric acid and heating the mixture for three-quarters of an hour on the water-bath. After it has become perfectly cold, filter off the salt, and wash it with dilute hydrochloric acid and alcohol. Yield, 30 to 34 grams, which is nearly the theoretical quantity.

Since nickel does not form any similar salt, this gives a means of preparing a nickel-free product from impure cobalt preparations.

Reactions. A cold, concentrated, aqueous solution of the above salt when treated with hydrochloric acid yields short, red crystals after standing some time. Mercuric chloride causes the immediate precipitation of long, rose-red needles of the composition $[Co(NH_3)_5Cl]Cl_2 \cdot 3\ HgCl_2$. Potassium chromate gives brick-brown crystals. Potassium dichromate causes the slow formation of clusters of fine, orange needles, or of large, flat prisms; ammonium oxalate slowly yields well-formed, red prisms which can be seen under the microscope.

132. Sulphate and Nitrate of the Chloropentammine Series.

Acid Chloropentamminecobaltic Sulphate, $[Co(NH_3)_5Cl]_2(HSO_4)_2SO_4$. Triturate 5 g. of chloropentamminecobaltic chloride with 12 g. of concentrated sulphuric acid in a mortar, whereby hydrogen chloride is evolved. Dissolve the mass in 40 c.c. of water at 70° and filter. On cooling the solution, long, thin, fuchsine-red prisms are deposited. The crystals become larger if they are allowed to stand for several days in contact with the mother-liquor, because smaller crystal grains are slightly more soluble than larger ones and therefore dissolve slowly, while the larger crystals grow still larger. Wash the crystals with absolute alcohol and dry them in the hot closet. Yield, 3 grams.

When the alcoholic washings are added to the mother-liquor a fine, dull-red, crystalline meal of the same salt is precipitated.

Dissolve it in a little warm water, cool the solution and precipitate the nitrate by adding concentrated nitric acid (Mass-action). Recrystallize in order to obtain a purer product. Small dull-red crystals.

Reactions. The aqueous solution of the pure sulphate gives no precipitate when treated with silver nitrate at the room temperature; on heating, however, some silver chloride is thrown down, but even on boiling, the reaction is incomplete. On the other hand, the sulphate radical, not being contained in the complex, gives at once a quantitative precipitation with barium chloride. The nitrate shows a similar behavior towards silver ions; the solution becomes turbid only on boiling.

In the analysis of the salt, chlorine and sulphate are determined after the substance has been decomposed by boiling with caustic soda; cobalt is weighed as sulphate after igniting the salt and heating the residue with concentrated sulphuric acid; ammonia is estimated in the usual manner by distilling with caustic soda and titrating the distillate.

133. Hexamminecobaltic Salts, $[Co(NH_3)_6]X_3$ (Luteocobalt Salts).

1*a*. *Luteocobalt Chloride.* Place 10 g. of chloropentamminecobaltic chloride, 8 g. of ammonium chloride, and 100 c.c. of 20% ammonia solution in a soda-water bottle (pressure-flask), and stopper it tightly. Wrap the bottle firmly in a towel, fasten it to a wooden handle and heat it for six hours in a pail of boiling water, shaking thoroughly once every two hours. Since a strong pressure prevails in the bottle, this part of the process should be carried out outside of the general laboratory, and before each shaking the mixture should be removed from the bath and allowed to cool somewhat. At the end of the heating the chloropentammine salt must have disappeared almost entirely. When cold open the bottle, pour the contents into an evaporating dish, and let it stand 24 hours in the open air, or under the hood, to allow the ammonia to volatilize. Dilute with 300 to 400 c.c. of water, add 50 c.c. of concentrated hydrochloric acid and heat the mixture in a flask for an hour on the water-bath. Add 250 c.c. more of concentrated hydrochloric acid and cool rapidly, while shaking, under the water-tap. Drain the yellow precipitate on a hardened filter paper and wash it with 20% hydrochloric acid.

To purify the first product, dissolve it in as little cold water as possible (about 5 g. of the chloride dissolves in 100 c.c. of water), filter the solution from any residual chloropentamminecobaltic chloride, and precipitate the yellow filtrate (keeping the liquid cold) by the gradual addition of half its volume of concentrated hydrochloric acid. Yield, 8 to 10 grams.

1*b*. The following method may be used to prepare large amounts of luteocobalt chloride: Prepare as concentrated a solution as possible of 100 g. crystallized cobalt chloride and 30 g. of ammonium chloride and add 20% ammonia until the precipitate first formed has redissolved. Prepare an ammoniacal silver chloride solution by precipitating silver chloride with NH_4Cl from 75 g. $AgNO_3$ and dissolving the precipitate in 20% ammonia. Mix the latter solution with the cobalt salt solution and leave the whole for 24 hours at 40° or two days at room temperature. Collect the precipitate, which is a mixture of metallic silver and luteocobalt chloride, on a filter and extract from it the luteo salt with water at 25°. Heat the extract on the water bath to 80° and add concentrated HCl until a permanent turbidity just appears; then cool the mixture by shaking it under the water tap. The desired preparation thereby crystallizes out perfectly pure. The silver residues are easily worked up to serve for further quantities of this preparation.

By cautiously acidifying the ammoniacal filtrate from above with repeated small portions of concentrated HCl (avoid much heating) additional luteo salt may be obtained contaminated with silver chloride and purpurcocobalt chloride. This may be purified as in 1*a*. Total yield, about 80 grams. As by-product about 15 grams of purpureocobalt chloride.

Reactions. A cold, saturated, aqueous solution of the luteochloride when treated with ammonium oxalate yields the very difficultly-soluble oxalate which consists of small, light-brownish-yellow, irregular crystals. With mercuric chloride a voluminous, light-pink double salt, $[Co(NH_3)_6]Cl_3 \cdot 3HgCl_2 \cdot H_2O$, is at once thrown down. Potassium chromate immediately precipitates brownish-yellow clusters of needles. Potassium dichromate causes the immediate formation of a precipitate which under the microscope is seen to be crystalline.

2. *Luteocobalt Nitrate by the Iodine Method.* Dissolve 24 g. of cobalt carbonate by warming it with a barely sufficient amount of

dilute nitric acid, filter, and dilute the solution to 100 c.c. Add 200 c.c. of concentrated ammonia, heat the solution to boiling, and oxidize the salt by adding 25.4 g. of iodine, which must be introduced slowly at first. A vigorous reaction takes place and a pale yellowish-brown precipitate of luteo salt is formed. All the iodine should be added in the course of half an hour. Allow the liquid to cool and after it has stood about two hours filter off the precipitate and wash it with water containing ammonia. Then boil the salt with 200 c.c. of approximately 56% nitric acid, whereby iodine is set free which can be recovered to some extent by means of two funnels, one placed in the flask and the other inverted over it to form a double cone. When all the iodine has been expelled, filter off the precipitate, drain it with suction, wash it with water containing nitric acid and finally with alcohol, and dry it in the hot closet. Yield, about 22 grams.

134. Aquopentamminecobaltic Salts, $[Co(NH_3)_5H_2O]Cl_3$ (Roseocobalt Salts).

Chloropentamminecobaltic chloride dissolves in ammonia, forming aquopentamminecobaltic chloride. If this solution is precipitated hot with hydrochloric acid, the chloropentammine salt is formed again, but if the hydrochloric acid is added slowly and the solution kept very cold, aquopentamminecobaltic chloride separates. Less care need be taken in the preparation of the difficultly-soluble aquopentamminecobaltic oxalate. Aquopentammine salts are also formed by the oxidation of hexamminecobaltous salts by potassium permanganate.

1. Dissolve 10 g. of chloropentamminecobaltic chloride in a liter flask by shaking it with 300 c.c. of 5% ammonia and heating upon the water-bath. Filter, if necessary, and then cool the solution to about 0°, first by holding the flask under running water and then by surrounding it with ice. While rotating the flask and keeping its contents cold, add strong hydrochloric acid from a dropping-funnel, a few drops at a time, until the solution reacts acid. Filter and drain the bright-red, crystalline precipitate; wash it first with a little 50% alcohol then with pure alcohol and dry it in a fairly warm place. Yield, 10 grams.

2. To a cold solution of 20 g. crystallized cobaltous chloride in 360 c.c. of water, contained in a 1500 c.c. flask, add 110 c.c. of concentrated ammonia and then 10 g. of potassium permanganate dissolved in 400 c.c. of water. Shake the mixture a

number of times, and, after it has stood for 24 hours, filter off the slime of hydrated manganese dioxide. Neutralize the filtrate with dilute hydrochloric acid, and, while keeping it cold by surrounding the vessel with ice, precipitate the product by the gradual addition of a mixture of three volumes of concentrated hydrochloric acid and one volume of alcohol. Wash the precipitate with alcohol. Yield, 12 to 15 grams.

3. *Purification of Aquopentamminecobaltic Chloride.* Dissolve the crude product, prepared according to either 1 or 2, in cold, 2% ammonia, using 75 c.c. for each 10 g. of the salt; filter off the slight residue of luteo salt, and, while keeping the solution cold with ice, precipitate the roseo salt by the gradual addition of concentrated hydrochloric acid. Drain the precipitate and wash it with a mixture of equal parts concentrated hydrochloric acid and water, then with alcohol, and dry it in a warm place.

4. *Aquopentamminecobaltic Oxalate.* Dissolve 10 g. of chloropentamminecobaltic chloride in a flask with 75 c.c. of water and 50 c.c. of 10% ammonia, heating on the water-bath. After cooling the deep-red solution to the room temperature, filter it and treat with a solution of oxalic acid until a precipitate begins to form, then continue to add the reagent very carefully until the solution is just acid. Filter, and wash the salt with water.

To purify the product, dissolve it as directed under 3, and reprecipitate the salt by the careful addition of oxalic acid solution. Drain the precipitate, wash it with water, then with alcohol, and dry it in a warm place. Yield, 9 grams of pure[1] substance.

5. *Aquopentamminecobaltic Chloride from Aquopentamminecobaltic Oxalate.* Cover 10 g. of aquopentamminecobaltic oxalate at room temperature with 30 c.c. of water and dissolve the salt by the addition of 50 c.c. of normal hydrochloric acid. Cool the solution with ice to about 0° and precipitate it very slowly by allowing 100 c.c. of concentrated hydrochloric acid to flow upon it drop by drop. Drain off the bright red precipitate and wash it first with hydrochloric acid diluted to one-half and then with alcohol. Yield, about 8 g. of perfectly pure aquopentamminecobaltic chloride.

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[1] The separation of luteo salt present as impurity is here more complete than according to procedure 3, because its oxalate is much more insoluble than its chloride.

Aquopentamminecobaltic chloride changes slowly on long keeping into chloropurpureocobaltic chloride.

135. Dibromotetramminecobaltic Bromide, $[Co(NH_3)_4Br_2]Br$ (Dibrompraseo Salt).

Place 20 g. of carbonatotetramminecobaltic nitrate in a flask, shake it with 80 g. of concentrated hydrobromic acid (cf. No. 35) and continue to shake while heating slowly over a free flame. The mass evolves a large amount of carbon dioxide and changes at first to reddish-brown, then pale-brown, and finally to a dull-green. When the color ceases to change, allow the mixture to cool to room temperature and add 50 c.c. of cold water, which serves to dissolve a little admixed bromoaquotetramminecobaltic bromide. Drain the precipitate on a hardened filter and wash it with cold water until the filtrate is no longer reddish-violet but comes through colorless. Yield, 24 grams of a very fine, light-yellowish-green, difficultly-soluble powder.

Dissolve a portion of the powder in warm, dilute ammonia, acidify with hydrobromic acid, and heat for half an hour on the water-bath. The salt is thereby transformed into bromopentamminecobaltic bromide, $[Co(NH_3)_5Br]Br_2$, which is a very finely granular, reddish-violet precipitate.

136. Dinitritotetramminecobaltic Salts, $[Co(NH_3)_4(NO_2)_2]X$ (Flavocobalt Salts).

Flavocobalt Nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3$. Dissolve, without heating, 10 g. of carbonatotetramminecobaltic nitrate in a mixture of 100 c.c. water and 14 g. of 40% nitric acid (sp. gr. 1.25), whereby a blood-red solution of diaquotetramminecobaltic nitrate is obtained. Add 20 g. of crystallized sodium nitrite to this solution, little by little, and place the flask containing the mixture in a bath of boiling water for 7–8 minutes, or until the color of the solution has become deep brownish-yellow, then immediately cool under the water tap and add 130 c.c. more of the 40% nitric acid. This causes foaming and a strong evolution of nitric oxide. The next morning, drain off the precipitate of mixed acid and neutral flavonitrate and wash it first with a little nitric acid and then with alcohol. Yield, 8–9 grams.

To purify the salt, recrystallize from 25 c.c. of water slightly acidulated with acetic acid. Collect the light-brown, crystalline flakes, or prisms, which are obtained, and wash with 50% alcohol, then with pure alcohol, and dry at a gentle heat. Yield, 6.5 grams.

Reactions. A cold, saturated solution of flavonitrate (3 g. in 100 c.c. water) gives with potassium chromate a crystalline precipitate of irregularly indented leaflets which are crossed and branched at right angles (microscope). With potassium dichromate small clusters of fine needles are at once precipitated, which are inclined towards one another like the branches of a fir tree.

Flavocobalt Chloride, $[Co(NH_3)_4(NO_2)_2]Cl$. Dissolve 1 g. of flavonitrate in 30 c.c. of water, warming gently; add 2 g. of ammonium chloride and filter if necessary. Then gradually add 100 c.c. of alcohol to the mixture and after standing 24 hours filter off the small, deep-yellow crystal leaflets. Wash the product with dilute alcohol, then with pure alcohol, and dry it in the hot closet. Yield, 0.9 gram.

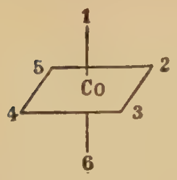
137. Dinitritotetramminecobaltic Chloride, $[Co(NH_3)_4(NO_2)_2]Cl$ (Croceocobalt Chloride).

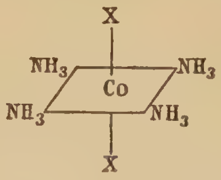
To a cold, filtered solution of 100 g. ammonium chloride and 135 g. sodium nitrite in 750 c.c. water, add 150 c.c. of 20% ammonia and 90 g. of cobaltous chloride dissolved in 250 c.c. of water. Draw air through this solution (cf. No. 108) for four hours, whereby the color, which is at first a pale, brownish-green, changes to green with a tinge of yellow, and a precipitate is formed. After standing for 12 hours filter off this precipitate and wash it with water until the last washing, on being treated with ammonium oxalate, stirred, and allowed to stand for some time, shows no precipitation. To purify the product which still contains some nitrate, divide it first into portions of 20 grams; then dissolve each portion in 40 c.c. of hot water containing a little acetic acid, filter the solution quickly through a plaited filter and immediately precipitate the salt from the filtrate by adding a solution of 40 g. ammonium chloride. Cool the mixture and after letting it stand 24 hours, filter off the yellow crystals, wash them with 90% alcohol until the washings barely give a test for chloride, then with pure alcohol, and dry the product in a desiccator. The yield is variable.

Reactions. A cold solution of croceochloride on being treated with potassium chromate gives a yellow precipitate of short, blunt crystals; with potassium dichromate there appears (but only after shaking some time) a deposit of short leaflets which are frequently grouped together in the form of stars (microscope). On being treated with nitric acid, yellow, feathery crystals of the difficultly-soluble nitrate are formed (0.25 g. of the latter dissolve in 100 c.c. of water at the room temperature).

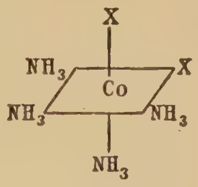
138. Comparison of the Isomeric Dinitritotetramminecobaltic Salts.

The difference between the flavo and croceo salts, in both of which the complex has the same empirical formula, $[Co(NH_3)_4X_2]$, can be explained according to Werner's theory by assuming that the substituents in the "inner sphere" are arranged differently in space. It is evident that if the constituents of the complex are placed around the central cobalt atom somewhat as the corners around the middle point of an octahedron, there are two possible arrangements; either the two constituents, X, which are different from the other four, are arranged opposite to one another and are connected by the hypothetical axis of the octahedron (trans-position), or they are situated side by side and are joined by one edge of the octahedron (cis-position). If the corners of the octahedron are numbered from one to six, as shown below, then the first arrangement may be designated as 1 · 6 and the latter as 1 · 2.





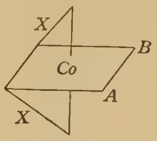
1, 6: trans-position

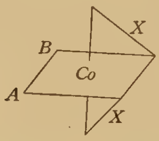


1, 2: cis-position

The usefulness of the above conception of isomerism is shown, among other ways, by the fact that it does not allow isomers to exist of the complexes in which only one of the substituents is different from the others; in reality no such isomers have been observed. It has been found that the croceo salts correspond to the trans arrangement, the flavo salts to the cis arrangement. The praseo salts belong to the trans series.

It is of fundamental importance with respect to Werner's conception of the structure of complex cobalt compounds, that it has been found possible to prepare isomers capable of rotating the plane of polarized light in opposite directions, *optical isomers* as they are called.[1] According to van't Hoff, optical isomerism is caused by the fact that the atoms are arranged in the molecules so that one compound is the mirror-image of the other, just as the right hand is opposite to the left in the arrangement of the fingers; one cannot be superimposed upon the other. Only in such a case can there be optical isomerism. When, therefore, optical isomerism is detected there must exist a corresponding spacial grouping of the atoms. The following drawings show how this can be with a complex molecule containing a cobalt atom around which the other atoms are grouped





A. *Both Salts are Tetrammine Compounds.* Dissolve some of each salt separately at the laboratory temperature in concentrated sulphuric acid and allow the deep-violet solutions to stand for 12 hours. Then add to each, while cooling with ice, somewhat more than an equal volume of concentrated hydrochloric acid, drop by drop, until the further addition causes merely a slight effervescence. Two days later decant the liquid from the small, glistening, green crystals, shake the latter with alcohol, drain them on a hardened filter and wash them with more alcohol. Both preparations are identical and consist of dichlorotetramminecobaltic acid sulphate (praseo salt). To establish the identity, transform each portion either into chloropentamminecobaltic chloride (1) or into chloroaquotetramminecobaltic chloride (2).

1. Dissolve small portions of each preparation in dilute ammonia by heating gently. Add concentrated hydrochloric acid little by little to the purplish-red solutions and then heat for half an hour on the water-bath. This brings about an almost quantitative separation of chloropentamminecobaltic chloride in the form of minute crystals which can be identified by the reactions given in No. 131.

2. Dissolve a small portion of each of the praseosulphate preparations in water by heating gently, and when the solutions have turned a deep, violet-red, which takes place after standing for some time in the cold or more quickly if warm, add an equal volume of alcohol and some concentrated hydrochloric acid. Let stand for

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[1] A. Werner, Ber. **44**, 1887 (1911) and subsequent papers.

12 hours more and then collect the precipitate on a filter. The chloroaquotetrammine salt is very similar externally to the chloropurpureo salt, but differs from it in the following reactions: mercuric chloride gives well-formed crystals only after standing for some time; potassium chromate and dichromate likewise yield precipitates only after long standing, or not at all.

B. *Distinguishing Reactions.* Boil small portions of the salts, each with 1 c.c. of concentrated hydrochloric acid. The flavo salt gives a green precipitate of praseo salt and the solution acquires a bluish color. The croceo salt, on the other hand, gives a dull-red precipitate of chloronitritotetramminecobaltic chloride.

To prepare somewhat larger amounts of these last substances, dissolve 0.5 g. of the flavo or croceo salt in 10 c.c. of concentrated hydrochloric acid. After 12 hours filter, drain and wash the precipitate, first with hydrochloric acid diluted with an equal volume of water, and finally with alcohol. Yield, 0.4 g. of each. The chloronitritotetramminecobaltic salt dissolves readily in 35 c.c. of cold water and recrystallizes upon the addition of 70 c.c. of concentrated hydrochloric acid to the filtrate. The praseo salt, which decomposes very easily, can be recrystallized by dissolving it quickly in about 200 c.c. of cold water, cooling the filtrate with ice and salt, and slowly introducing 70 c.c. of concentrated hydrochloric acid.

139. Trinitritotriamminecobalt, $[Co(NH_3)_3(NO_2)_3]$.

Dissolve 45 g. of crystallized cobalt chloride in 125 c.c. of water. Dissolve 50 g. of ammonium chloride and 67 g. of sodium nitrite without heating in 375 c.c. of water and add this, together with 250 c.c. of 20% ammonia, to the first solution. Conduct a rapid current of air through the mixture for four hours (cf. No. 108). Divide the thick brown solution in three evaporating dishes and allow it to stand three days in the open air or under the hood. Filter off the crystals which separate and wash them with cold water until the washings are nearly free from chloride. Yield, about 35 g.

Divide the crude product between two filters and extract it with 1.0 to 1.25 liters of hot water containing a little acetic acid. On cooling, yellow to yellowish-brown crystals of trinitritotriamminecobalt separate from the clear filtrate. Yield, 20 to 25 g.

Solutions of this substance do not conduct the electric current nor do they give precipitates with mercuric chloride, with oxalates, or with chromates.

140. Hexamminechromic Nitrate, $[Cr(NH_3)_6](NO_3)_3$ and Chloropentamminechromic Chloride, $[Cr(NH_3)_5Cl]Cl_2$.

Anhydrous chromic chloride, when in contact with liquid ammonia, takes up partly five and partly six molecules of ammonia. The hexammine salt dissolves readily when the mixture is treated with cold water, and from the filtrate the nitrate can be precipitated by the addition of nitric acid. The chloropentammine chloride, on the other hand, does not dissolve in the cold water, but can be purified by suitable recrystallization.[1]

Chloropentamminechromic chloride (chloropurpureochromic chloride) furnishes an excellent illustration of the fact that the characteristic properties of these complex compounds are often less influenced by the nature of the metal present than by the type of combination. Chloropurpureochromic chloride is so similar to chloropurpureocobaltic chloride that it is necessary to decompose the substances completely in order to prove that the metal is different.

Generate ammonia by heating 500 g. of concentrated ammonia solution on a Babo funnel, dry the gas by passing it through two towers filled with lime and through a U-tube containing sodium hydroxide, then condense it to a liquid in an Erlenmeyer flask containing 8 g. of finely powdered, anhydrous chromic chloride (No. 43). In order to exclude carbon dioxide from the condensing flask, this must be closed with a stopper and provided with an inlet and an outlet tube. For the cooling agent use a mixture of carbon-dioxide-snow and ether (temperature about $-80°$) placed in a small beaker, which in turn is placed within a larger beaker so that an inclosed air space between the glass walls shall act as an insulator.

When the chromic chloride has combined with the liquid ammonia, forming a reddish-brown mass, stop the operation and allow the excess of ammonia to evaporate from an open dish. Triturate the residue with 30 c.c. of ice-cold water, filter and wash the undissolved salt with a little cold water until the filtrate runs through of a reddish color. Add concentrated nitric acid to the filtrate, which precipitates luteo-chromic nitrate. Again filter, dissolve the salt in a little warm water containing a few drops of nitric acid, and, by the addition of more nitric acid, precipitate out the crystalline hexamminechromic nitrate. Yield, about 7 g.

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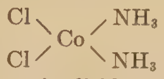
[1] For a method of preparing chloropurpureochromic chloride without the use of liquid ammonia, cf. O. Christensen; J. pr. Chem. (2) **23**, 54 (1881) and S. M. Jörgensen, *ibid.* **20**, 105 (1879).

The residue from the treatment with ice water consists of chloropurpureochromic chloride. Boil it in a beaker with concentrated hydrochloric acid, cool, add some water, collect the salt on a filter and wash it with a little cold water. Then dissolve the salt as quickly as possible at 50° in 400 to 500 c.c. of water containing a few drops of sulphuric acid. Filter the solution at once through a large plaited filter and add an equal volume of concentrated hydrochloric acid. Allow the beautiful red crystals which separate to stand an hour in contact with the mother-liquor, then drain them and wash first with 20% hydrochloric acid (1 pt. conc. HCl : 1 pt. H_2O), then with alcohol, and dry the product in a desiccator. Yield, about 5 grams.

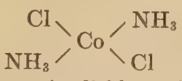
Transformation of the Luteo Salt into Chloropurpureo Salt. Mix a solution of hexamminechromic nitrate, dissolved in eleven times its weight of hot water, with an equal volume of concentrated hydrochloric acid and boil gently for from thirty minutes to an hour. When the liquid has become cold, filter off the precipitated chloropentammine chromic chloride and wash it as above.

141. Hexamminecobaltous Chloride, $[Co(NH_3)_6]Cl_2$.

In compounds with a coördination number 4, if the substituents are supposed to be at the corners of a square lying in a plane passing through the central atom, there is, according to Werner, a possibility of isomerism. Thus, if the outlying groups consist of two unlike pairs, stereoisomerism will take place, if, in one case, the two like groups are side by side in neighboring corners of the square and in the other case the like groups are opposite to one another, as at the ends of a diagonal of the square. The classic example of this kind of isomerism is found in *trans*-diamminechloroplatinum and *cis*-diamminechloroplatinum, which have been known for a long time as "chloride of Rieset's second base" and "Pyrone's salt." More recently[1] perfectly analogous derivatives of bivalent cobalt have been prepared, α- and β-diamminedichlorocobalt, which have different colors and are characterized by different ammonia tensions. The pink alpha compound is the more stable and probably corresponds to the cis-formula:



α-diamminedichlorocobalt
pink



β-diamminedichlorocobalt
blue

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[1] W. Biltz and B. Fetkenheuer, *Z. anorg. Chem.* **89**, 121 (1914).

The preparation of these two isomeric compounds is described in Preparations 142 and 143. Both of these can be obtained from hexamminecobaltous chloride, which, as described here, is prepared in much the same way as the analogous nickel salt (No. 128).

Before beginning the experiment proper, prepare some air-free alcoholic ammonia solution. Boil 200 c.c. of alcohol, in a flask connected with a reflux condenser, for half an hour, then remove the condenser and pass a current of dry ammonia into the alcohol while it is cooling. Take the ammonia from a bomb or generate it as in Preparation No. 140.

Dissolve 15 g. of cobaltous chloride crystals, $CoCl_2 \cdot 6H_2O$, in 15 c.c. of water and boil the solution to expel all air. While still hot, pour this solution into 40 c.c. of hot, concentrated ammonia solution. Filter immediately into a 150 c.c. Erlenmeyer flask using a 12 cm. filter which has been moistened with concentrated ammonia solution and letting the funnel hang in the neck of the flask to avoid contact of air with the filtrate. Keep the filtrate hot, over a burner, and add enough of the alcoholic ammonia solution to form a slight permanent turbidity. The flask will now be practically full of liquid; close it loosely with a cork stopper and cool under running water; tiny, pink, octahedral crystals of hexamminecobaltous chloride will form. To collect the precipitate, it is best to use a small filter tube containing a perforated porcelain plate covered with a flat piece of filter paper. A large Gooch crucible and paper filter can be used if preferred but a Büchner filtering funnel is less satisfactory because there is too much exposure to the air. Wash the precipitate once with concentrated, aqueous ammonia solution, three times with alcoholic ammonia solution and finally with ether, keeping the crystals covered with liquid throughout the washing operations. Finally, apply strong suction for a moment, remove the crystals to a vacuum desiccator and dry over soda lime to which a little powdered ammonium chloride has been added. The color of the crystals should be a pale, yellowish-pink. A deeper yellow or brown color shows that oxidation has taken place.

Yield, 7 g. A better yield can be obtained if the ammoniacal cobalt solution is completely precipitated with the alcoholic ammonia, but the crystals are then so small that they are very susceptible to atmospheric oxidation and are hard to wash thoroughly.

142. α-Diamminedichlorocobalt, α-[$Co(NH_3)_2Cl_2$].

The more stable of the two isomers mentioned in the introduction to Preparation No. 141 can be prepared as equilibrium product by thermal decomposition of the hexammine. At about 150° the hexammine has an ammonia tension of considerably more than an atmosphere whereas the ammonia tension of the diammine corresponds to only 10–20 mm.

Transfer about 2 g. of dry hexamminecobaltous chloride with the aid of a short, dry funnel, to a dry, weighed test-tube, taking care that none of the crystals adhere to the sides of the tube. Weigh the tube and its contents to an accuracy of 4 significant figures. Stopper the tube with a vacuum-tight, rubber stopper carrying a right-angled piece of glass tubing with a glass stopcock. Connect this tubing with a short-armed manometer and beyond the latter with the outlet-arm of a 100 c.c. distilling flask, placing a screw-cock between the manometer and the distilling flask. Fill the distilling flask about one-third full of concentrated sulphuric acid for absorbing ammonia, insert a rubber stopper carrying glass tubing that reaches almost to the surface of the sulphuric acid and make connection through a rubber tube with a screw-cock with the suction pump. Evacuate the entire apparatus down to a pressure of 10–15 mm., close the stopcock at the test-tube and dip the tube in a bath of melted paraffin or sulphuric acid at 150°. Immediately after placing the tube in the hot bath, open the glass stopcock very slowly and apply suction for one minute to withdraw the ammonia. The latter is given off very vigorously at the start and, if the stopcock is opened too quickly, powdery solid material will be carried along with the gas. The color of the solid changes from pink to blue, the latter being the color of the unstable diammine. Close the stopcock and allow the tube to remain in the hot bath at 150° for half an hour to give the unstable diammine time to change to the stabler modification. Then carefully open the stopcock again, apply a little more suction and again allow the stoppered tube to remain quietly in the bath for a half hour. Repeat this treatment two or three times until a pure, pink-colored salt is obtained. Then, if the decomposition has been complete, on closing the screw-clamp between the manometer and the sulphuric acid, which was used to absorb escaping ammonia, a pressure of about 40 mm. will be shown in the manometer. If some undecomposed hexammine remains, the pressure will be much greater. Weigh the tube and its contents as a further proof that the change has been completed.

143. β-Diamminedichlorocobalt, β-$[Co(NH_3)_2Cl_2]$.

The unstable β-diamminedichlorocobalt can be obtained by careful decomposition of the hexamminecobaltous chloride (cf. Nos. 141 and 142) at a fairly high temperature, as the primary decomposition product.

Place about 2 g. of hexamminecobaltous chloride in the apparatus used in the preceding preparation. Weigh the substance taken to 4 significant figures. Heat the contents of the test-tube to 72° but in this case pump off the ammonia continuously until there is no more of the undecomposed hexammine discernible with the aid of a lens and the substance appears a pure light blue in color (about 2 hours). From time to time, tap the test-tube and shake it a little so that the entire powder is uniformly heated. Finally, weigh the tube and its contents again, to prove that the decomposition is complete.

Transformation of β- into α-diamminedichlorocobalt. In order to show, even more clearly, that the beta salt is less stable than the alpha, and to illustrate the transformation, place a few milligrams of each diammine in separate glass tubes of about 15 cm. length and 6 mm. internal bore. Evacuate both tubes and seal them by softening the glass with a flame and drawing out the glass. Suspend both of the sealed tubes in a bath at 180° which can be done conveniently if a little glass hook is made at the top of the tubes when they are being sealed. After about an hour it will be found that the blue diammine has become pink while the pink diammine has remained unchanged.

The experiment succeeds even in open tubes but the change does not show as convincingly.

HYDRATES.

The hydrates formed by crystallization from aqueous solutions vary in composition with the temperature and concentration of the solution. A systematic determination of the hydrates which a compound can form, as well as of the conditions under which they can exist, can be carried out in the light of the principles of heterogeneous equilibrium.

1. Thermic Analysis. If the freezing-point of an aqueous solution of a salt is determined at various concentrations and the results are plotted with the temperatures as ordinates and with the concentrations in per cent as abscissas, a curve *AC* is obtained which starts at the freezing-point of pure water and descends in accordance with the law of Raoult and van't Hoff (Fig. 23). The highly concentrated solutions, on the other hand, are to be regarded as solutions of water in the salt; the curve *CB* shows the region in which the freezing-point rises as the amount of water diminishes until finally the freezing-point (or melting-point) of the pure salt is reached. In the region of the first curve, that part of the mixture which acts as solvent crystallizes out on freezing, — in this case pure ice; in the region of the second curve, the solid salt is deposited as the solution cools. The point where these two curves intersect is called the *eutectic point*, and is characterized by the fact that salt and ice crystallize simultaneously in an intimate, eutectic mixture. Such mixtures, which are also known as *cryohydrates*, possess freezing (or melting) points which are constant, and are lower than the freezing-point of pure water; they are on this account used for maintaining uniform temperatures of below zero centigrade.

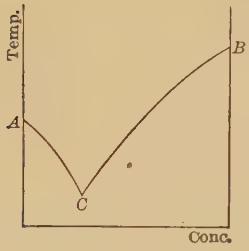

Fig. 23.

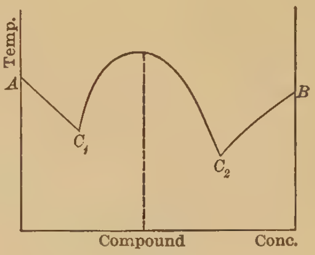

Fig. 24.

If the salt employed forms a chemical compound with water, then the two systems *water/hydrate* on the one hand and *hydrate/anhydrous salt* on the other hand are each to be considered independently, according to the principle just outlined. If, as before, the concentrations are plotted as abscissas and the temperatures as ordinates, a double pair of curves is obtained with two eutectic points. The two inside curves unite in a common maximum which is the freezing-point of the pure hydrate (Fig. 24). Conversely it is clear that by determining the freezing-points of a complete series of mixtures of the salt and water, the presence of a hydrate can be detected by the appearance of a maximum on the curve, and its composition can be read by dropping a perpendicular from the maximum point to the horizontal axis. Several maximum points indicate the presence of several hydrates. In this way Roozeboom has, for example, proved in the case of ferric chloride the existence of the hydrates $2FeCl_3 \cdot 4H_2O$. $2FeCl_3 \cdot 5H_2O$, $2FeCl_3 \cdot 7H_2O$, $2FeCl_3 \cdot 12H_2O$.

This method of analysis does not apply solely to the mixtures of a salt and water, but it can be used very generally to prove the existence of compounds. It has acquired a high importance in the study of alloys (Tammann and his students: see articles in Z. anorg. Chem. mostly later than 1903).

2. Vapor Tension Analysis. When a hydrated crystallized salt is in equilibrium with water vapor, its water of hydration can be progressively withdrawn in the same manner that ammonia is withdrawn from the metal ammonia compounds (cf. p. 163). Two methods are available by which salts can be investigated from this point of view. According to the first the vapor pressure of the salt is determined for varying water content, and a curve is constructed with the aqueous tensions as ordinates and the corresponding percentages of water as abscissas; if the salt forms a number of different hydrates, the vapor pressure above any given mixture of the hydrates remains constant, when water is slowly withdrawn, as long as any of the hydrate richest in water is still present. When this hydrate is entirely exhausted, the pressure sinks abruptly, and a second, and lower, horizontal line on the plot corresponds to the tension of the next lower hydrate, etc. (cf. Fig. 25). The tension of aqueous vapor in the case of hydrated cupric sulphate is given in the following table:

$CuSO_4 + 4.5\ H_2O$	46.3 mm.	$CuSO_4 + 1.5\ H_2O$	29.7 mm.
$CuSO_4 + 3.5\ H_2O$	47.1 "	$CuSO_4 + 0.5\ H_2O$	4.4 "
$CuSO_4 + 2.5\ H_2O$	29.9 "		

From this we may conclude that the following hydrates exist: $CuSO_4 \cdot 5\ H_2O$; $CuSO_4 \cdot 3\ H_2O$; $CuSO_4 \cdot 1\ H_2O$. The vapor pressure of the pentahydrate is about 46 mm. and remains constant, irrespective of the amount present, until the pentahydrate has entirely disappeared. Then the pressure drops to that of the trihydrate (about 30 mm.), and again remains constant until this is completely changed into monohydrate (vapor pressure about 4.5 mm.).

The other method of vapor tension analysis consists in determining the decomposition temperature under a constant pressure of aqueous vapor (cf. p. 163). Approximate values for the decomposition temperature can be obtained, however, by finding the point at which water is given up when the salt is heated in any indifferent atmosphere. In this way crystallized copper sulphate loses the last molecule of water at 220° to 240°, and from this and the fact that the other molecules of water escape at much lower temperatures, the existence of a definite monohydrate has been recognized for a long time.

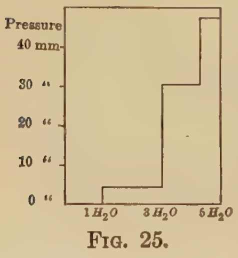

Fig. 25.

In the cases where the water is not chemically bound in a compound, but is merely adsorbed (cf. pp. 41 and 44), either of these methods of investigation shows merely a continuous loss of water with rising temperature, or diminishing pressure.

The question as to how the water is united with the components of the salt can be answered only in a few special cases. Undoubtedly in certain metal-ammonia compounds it belongs to the complex, positive component of the salt, (cf. especially No. 134). Probably the water is also attached to the metal atom as one of the constituents of the complex in such of the hydrated salts as are closely related to the metal-ammonia salts in their stoichiometrical composition. For example, cupric sulphate hydrate is analogous to tetramminecupric sulphate (No. 126), whereas the violet modification of chromic chloride corresponds to the hexammine salts (No. 140):

$$[Cr(NH_3)_6]Cl_3$$
$$[Cr(NH_3)_5H_2O]Cl_3$$
$$[Cr(H_2O)_6]Cl_3.$$

The fact that the number of molecules of water in hydrated salts is frequently four or six is quite in accord with the views just stated, inasmuch as four and six are also the most usual coördination numbers. It cannot be claimed, however, that all compounds containing water of crystallization must possess complex cations; since, among other reasons, it is quite certain that the negative components of compounds have the power of attaching water molecules.

How much, and in what manner, water is united with the ions in solution is not positively known. A number of facts make it seem extremely probable, however, that the ions are hydrated.[1]

144. The Melting-point Maximum for Magnesium Nitrate Hexahydrate; Eutectic Mixture of Barium Chloride Dihydrate and Water.

1. The freezing-point diagram of a series of mixtures of anhydrous magnesium nitrate and water shows a pronounced maximum for the composition corresponding to that of the hexahydrate. Measurements from which such a diagram can be constructed can be made with the very simplest apparatus. Starting with the crystallized hexahydrate, one branch of the curve is obtained through successive additions of water, which by dissolving in the hexahydrate depresses its freezing-point; on the other hand, another branch of the curve is obtained by adding successive portions of a less hydrated magnesium nitrate which likewise dissolves in the hexahydrate and depresses its freezing-point. The two branches of the curve unite in a very pronounced maximum at the composition $Mg(NO_3)_2+6\,H_2O$. As a rule the maxima obtained in the investigation of hydrates are less pronounced, and often they are entirely concealed. Regarding the so-called "concealed maxima," see Tammann. A critical compilation of all the known equilibria between water and inorganic substances is given in Table 133, in Landolt-Börnstein-Roth's physikalisch-chemischen Tabellen, 4th edition, 1912.

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[1] E. W. Washburn. The Hydration of Ions. J. Am. Chem. Soc. **31**, 322 (1909); Hydrates in Solution; Review of Recent Experimental and Theoretical Contributions, Technology Quarterly, **1908**, 360, or Jahrbuch der Radioaktivität u. Elektronik, **1908**, December.

The method employed is the same in principle as that followed in determining freezing-points with the well-known Beckmann apparatus, but it is very much more simple because the freezing-points here measured are so far apart that an accuracy of between one and two degrees is sufficient. As container for the substance, a test-tube about 19 cm. long and 2 to 2.5 cm. wide suffices; as thermometer, one graduated in whole degrees and reading to 120° is suitable; an air-mantle is superfluous; as stirrer, a thin glass rod or a piece of iron wire bent into a suitable shape may be employed, although it is preferable to use a heavy platinum wire as in the Beckmann apparatus. As heating and cooling baths, two beakers of from 300 to 400 c.c. capacity, filled with paraffin oil and provided with heavy iron wire stirrers, are used. Weighings need be accurate only to two, or at the most three, significant figures.

Place about 12 g. of magnesium nitrate hexahydrate in the test tube and close the mouth with a stopper through which the thermometer and stirrer are inserted. Dip the tube well into the heating-bath, heat rapidly to 70°, and from that point on, more slowly. The melting point of the substance is shown, in the first place, by the disappearance of crystals, and, second, by the fact that the temperature remains for some time constant (89°). Next heat the bath to 110°–120°, transfer the test-tube to the cooling-bath, which has been brought to about 90°, and observe the point at which crystals begin to appear and the temperature ceases to fall during the crystallization; by repeating the experiment several times it is possible to establish very sharply the point at which the crystals appear or disappear. Now, from a weighed pipette, or from a small weighed wash-bottle, add one or two grams of water, and determine the amount added by a second weighing. Mix the mass well with the water, melt it completely, and determine as before the point where crystals begin to separate; it lies considerably lower. Follow the curve in this way by three or four similar experiments until the laboratory temperature is reached. The heating-bath should be, in every case, about 10° warmer and the cooling-bath 10° colder than the temperature which is to be measured, the latter being first determined by a preliminary rough experiment. As the concentration of the water increases, the points of constant temperature become less pronounced, but the beginning of crystallization can always be observed distinctly by the clouding of the liquid.

To establish the other branch of the curve, determine the freezing-points in a new series of mixtures: First, take a weighed amount (about 30 g.) of the hexahydrate, and free it from a part of its water of crystallization by heating it in an open dish upon the water-bath for five or six hours, or until the loss in weight corresponds to about 10%. Pour the sirupy liquid while still warm into a porcelain mortar, and stir it with a pestle while it solidifies. When cold, powder the porcelain-like mass and compute the amount of water present by igniting a weighed sample until it is completely changed to MgO. For the freezing-point determinations, commence as in the first series with the pure hexahydrate, and add successively portions of 1—3 g. of the partially dehydrated salt just prepared. After each addition, bring about complete solution by fusing the mixture, and then observe the point at which crystals begin to separate on cooling. More highly concentrated liquids are sirupy and become turbid on account of air bubbles, and thus the freezing-points are not so sharply defined; it is sufficient, however, to carry the observations to about 70° on this branch of the curve.

To construct the melting-point diagram, compute for each experiment the total amount of anhydrous magnesium nitrate present, the total amount of water, and from these the number of parts of anhydrous salt in 100 parts of the mixture. Plot the latter values as abscissas and the observed temperatures as ordinates. Between points corresponding to 42% and 58% of the anhydrous salt the curve rises from about 18° to 89°, whereas between 58% and 65% it falls from 89° to 70°. The maximum point of the curve corresponds to the hexahydrate, and it is thus proved thermo-analytically that this hydrate exists as a definite compound.

2. If the *magnesium-nitrate-hexahydrate/water* diagram were to be carried out to the freezing-point of pure water, it would show the existence of a second hydrate with nine molecules of water, and of a eutectic point at −29°, between the latter and pure water. The characteristics of the eutectic point are more conveniently studied in the case of the system *barium-chloride-dihydrate/water*.

Place 10 c.c. of water in the apparatus used above and determine the freezing-point; then add about 1 g. of crystallized barium chloride (weighing it to an accuracy of two significant figures), and determine the freezing-point of the solution with a thermometer which reads from – 20° to 100° and is graduated in whole degrees. Repeat the measurements with successive additions of 1 g. of the salt. As cooling-bath a mixture of ice and salt can be used at first. The solidification point is easily recognized by the temperature remaining constant, but this point is usually preceded by a supercooling of about 0.5° before crystallization is induced by vigorous stirring. When temperature equilibrium has been established, withdraw the test-tube from the freezing mixture in order to note the appearance of the separated solid. Pure water usually shows a crust of ice and large needles; the solutions show finely divided flakes of ice. If, in about the third experiment, the neighborhood of the eutectic point is reached, a freezing-point is at first observed as usual, but after the mixture has stood in the freezing bath for some time the temperature again falls until a second halting-point is registered at – 8.4°, and at this temperature opaque, white masses of the cryohydrate, consisting of ice and barium-chloride-dihydrate, separate. In the succeeding experiments the solidifying point rises rapidly since the region is reached in which the salt acts as the solvent for the water. The deposited substance now consists of barium-chloride-dihydrate which is easily distinguishable from ice. At the same time the halting-point on the thermometer becomes less distinct because the heat of solution of the salt is less than the heat of fusion of ice. It is possible, however, to determine very sharply, as in the magnesium nitrate series, the point at which crystallization begins; and this is especially true since the baths used in these experiments are of ice water, water at the room temperature, and finally liquid paraffin, instead of the opaque mixture of ice and salt. Each measurement is repeated several times, leaving a little of the barium salt undissolved each time to serve in starting the next crystallization. It is sufficient to carry the curve up to about 70° in three or four experiments. The temperature readings in the case of the first field (the ice curve) should be accurate to about 0.1°, and in the second field (solubility curve) to within one or two whole degrees.

The curve is plotted as before. Between 0% and 24% $BaCl_2$ the temperature of solidification falls from 0° to – 8.4°; between

24% and about 33%, it rises from − 8.4° to above 70°. If the eutectic point itself is not actually obtained in one of the experiments, it is easily found as the intersection point of the two curves.

145. Calcium Sulphate Hemihydrate.

Gypsum, as it occurs in nature, consists of calcium sulphate dihydrate. On heating gypsum, its aqueous tension increases until at 101.5° it is equal to the atmospheric pressure, and at 107° it is 970 mm. or the same as that of liquid water at the same temperature; in a closed tube, therefore, water and the dihydrate co-exist up to a temperature of 107°. At higher temperatures the dihydrate breaks down into the hemihydrate, $CaSO_4.\frac{1}{2}H_2O$, and water, but these recombine to again form the dihydrate when the tube is allowed to cool. In analogy with the transformation of allotropic forms into one another, the temperature at which the above reaction is reversible is known as the *transition point.*

Gypsum is dehydrated technically by heating the powdered mineral in iron kettles to about 130° while stirring. The product is the ordinary plaster of Paris, which consists of calcium sulphate hemihydrate, and which when mixed with water at a temperature below 107° takes up some of the latter to again form the dihydrate. This solidifies to a solid mass of interlocking crystal needles. The production of plaster casts is accomplished in this manner. When heated to 160°, gypsum becomes "dead burnt," or completely dehydrated, in which form it does not readily unite with water again.

The conversion of the dihydrate to hemihydrate can be effected below 107° if the aqueous tension is lowered by the presence of other substances. Thus under a saturated solution of common salt the hemihydrate is formed at 77°, and under a saturated solution of magnesium chloride at about 11°. The dehydration is effected very rapidly by heating gypsum in concentrated nitric acid (sp. gr. 1.4) on the water bath.

Prepare calcium sulphate dihydrate by adding 120 c.c. of 2-normal sulphuric acid to an aqueous solution of 50 g. of calcium chloride; wash the precipitate by decantation with water, and then with a little alcohol, and dry it in the hot closet. The product consists of small needles (Microscope). Mix 20 g. of the preparation with 50 c.c. of concentrated nitric acid (sp. gr. 1.4) so as to form a thick paste, and heat the mixture on the water-bath with occasional stirring. Watch the course of the transformation by removing a few drops of the mixture from time to time and examining it under the microscope; after about 10 minutes the finely pointed needles disappear, and compact prisms with right-angled outlines appear in their place. After half an hour cool the contents of the dish, allow the solid to settle, decant off the liquid as completely as possible, shake the residue with 50% alcohol, and filter at once with suction. Throw away the filtrate, wash the precipitate, and dry it in the hot closet. Yield, almost quantitative.

Determine the water content of the product by igniting a weighed sample to faint redness. The hemihydrate contains 6.2% water.

The hemihydrate prepared as above consists of larger crystals than commercial plaster of Paris, and for this reason it "sets" more slowly. Mix half of the preparation with water to form a thick paste, and allow it to stand until, at the end of about 30 minutes, solidification takes place. The process may be watched more closely by placing a few drops of the fresh mixture under the microscope; after about 20 minutes, fine needles of the dihydrate are seen to appear, and after that to increase rapidly in quantity while the compact prisms of the hemihydrate disappear. Simultaneously with the formation of the crystal needles under the microscope, the larger sample grows hard. This change may be compared with the similar transformation of potassium lead iodide (cf. No. 105). Moisten the remainder of the hemihydrate with a mixture of alcohol and water; this time the mass solidifies much more slowly because the vapor pressure of the water is diminished by the presence of the alcohol.

146. Hydrates of Sodium Sulphate. Supersaturated Solutions.

The solubility of ordinary, crystallized sodium sulphate, $Na_2SO_4 \cdot 10\,H_2O$, increases rapidly with rise in temperature, but can be followed only to 32.4° because at this temperature the solid decahydrate, standing in contact with the solution, is completely dehydrated. The solubility of the anhydrous salt is peculiar in that it diminishes with rise of temperature; thus at 32.4° the saturated solution contains the maximum amount of sodium sulphate. Accordingly, when a saturated solution is allowed to evaporate, the anhydrous salt separates if the temperature is above 32.4°, whereas the decahydrate is deposited if the solution is below this temperature. The solutions, however, can very easily become supersaturated, provided they are protected from dust, etc., which tends to start crystallization. By allowing such supersaturated solutions to remain in the cold, a different hydrate, $Na_2SO_4.7H_2O$, crystallizes spontaneously, but since this salt is more soluble than the decahydrate, the solution standing over it remains supersaturated with respect to the decahydrate.

Dissolve 170 g. of crystallized sodium sulphate in 75 c.c. of water at 32°, filter, and divide the solution equally among five small, clean flasks which have been freshly rinsed with distilled water. In filling the flasks take care not to wet the necks with the solution. Immediately stopper each flask with a loose plug of cotton. Allow two of the flasks to stand in the ice-chest over night, or longer, until the heptahydrate has crystallized out in large, closely packed crystals which fill about one-third the volume of the liquid. Allow the three other flasks to cool to room temperature; a thick, oily solution is obtained from which, although it is supersaturated, no crystals separate even when the liquid is gently rotated. Inoculate the first flask with a minute fragment of sodium sulphate, whereupon crystals at once begin to form at the point inoculated and grow rapidly until the whole contents of the flask have solidified. Place a trace of sodium sulphate upon a piece of filter paper, then brush it off as completely as possible. Tear off a piece of this filter paper and use it to inoculate the contents of the second flask. Open the third flask, and close it with the thumb, which has first been well rinsed with distilled water. If the thumb is perfectly clean and free from crystals of the salt and particles of dust, the solution will bear shaking without the appearance of crystals.

Introduce a trace of decahydrate into each of the two flasks which contain the deposited heptahydrate. The supernatant solution then crystallizes into the decahydrate so that the two hydrates are obtained together in the flask one above the other. After standing a long time, the more soluble heptahydrate goes over into the less soluble decahydrate.

147. Transition Point of Sodium Sulphate,

$$Na_2SO_4.10\,H_2O \rightleftarrows Na_2SO_4 + 10\,H_2O.$$

32.383°.

If a mass of crystals of sodium sulphate decahydrate is heated slowly, the temperature rises steadily until 32.383° is reached, at which point it remains constant for a considerable time, because the heat then received from the exterior is used entirely in dehydrating the salt. If the mixture of water and sodium sulphate is heated to a higher temperature and then allowed to cool slowly, the temperature again remains constant at the same point as long as the heat of hydration is sufficient to compensate the loss of heat to the surroundings. Compare the corresponding relations in the change in state of aggregation (No. 6, p. 15). Practical advantage may be taken of this behavior of hydrated sodium sulphate for producing and maintaining very accurately the temperature of 32.383°, as, for example, for a fixed point in thermometry. By placing a mixture of the anhydrous salt and the hydrate in surroundings of approximately 32 to 33°, the temperature of the mass adjusts itself sharply to 32.383°, and remains constant a very long time at this point, for if the external temperature is somewhat higher, the heat conducted into the mixture is absorbed in dehydrating the salt, whereas if the surroundings are cooler the temperature of the mixture is maintained by the heat liberated in the hydration of the salt. A bath composed of such a mixture, therefore, can be used as a very delicate thermostat.[1]

The transformation $MnCl_2 . 4 H_2O \rightleftarrows MnCl_2 . 2 H_2O + 2 H_2O$ takes place at 58.089° ± 0.005°. Richards and Wrede, Z. phys. Chem. **61**, 313 (1907).

Dissolve 100 g. of crystallized sodium sulphate in 50 c.c. of water at about 33°, filter the solution, and cause the salt to recrystallize by shaking the solution and cooling it under the water tap. Drain the crystalline meal on the suction filter, wash the salt once with a little cold water, and use it moist in the following experiment. Place about 12 g. of the crystals in a test-tube and insert a thermometer which is graduated in tenths, or fifths, of a degree. Place this test-tube inside a slightly larger one so that an air space of about 2 mm. separates their walls, and clamp the two tubes thus arranged so that they dip into a beaker containing about 600 c.c. of water. Keep the temperature of the water at 35° to 36°.

To prepare the equilibrium mixture in the inner test-tube, remove this from its air mantle, and dip it directly into the warm water in the beaker. When its contents are partly melted, wipe the tube and replace it in the larger tube. The transition temperature is quickly established, especially if the mixture is stirred, and remains constant for more than half an hour. By removing the inner tube and allowing it to cool somewhat, the mixture again assumes the transition temperature. Before every reading of the thermometer, the mass should be stirred.

The anhydride present in the mixture is recognized as a fine turbid powder in the presence of relatively large crystals of the decahydrate.

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[1] Cf. Richards, Z. phys. Chem. **26**, 690 (1898); Richards and Mark, *ibid*, **43**, 465 (1903).

148. Isomeric Chromic Chloride Hydrates, $CrCl_3 . 6 H_2O$.

Hydrated chromic salts possess both violet and green modifications. Although solutions of most of the green chromic compounds cannot be made to yield the crystallized salts, the chloride, on the other hand, can be crystallized in both forms, each having the same composition $CrCl_3 . 6 H_2O$. The violet salt is normal in its behavior, inasmuch as when it is dissolved in water the entire chlorine is ionizable, and the solution thus contains three chlorine ions to one hydrated chromic ion. The formula of the violet modification is therefore $[Cr(H_2O)_6]Cl_3$. On the other hand, the solution of the green salt contains chlorine in a non-ionic condition — according to Werner and Gubser,[1] two of the chlorine atoms are attached in the complex. Since, furthermore, two of the six molecules of water are less firmly bound in the salt than the other four, the green chloride may be formulated:

$$[Cr(H_2O)_4Cl_2]Cl . 2H_2O.$$

For further details, consult the original article cited in which the above explanation is deduced from conductivity measurements. It has been shown by Weinland and Koch[2] that precipitations with silver salts serve qualitatively but not quantitatively to explain the relations.

Preparation of the Crude Chloride. Warm 100 g. of chromic acid anhydride (under the hood in the hydrogen sulphide room) in a flask, with 400 g. of concentrated hydrochloric acid. Red vapors are first evolved. Boil the solution until it becomes pure green and no more chlorine is evolved. About three hours are required, and during the boiling more hydrochloric acid is added if necessary. Concentrate the solution in an evaporating dish until it has the consistency of sirup, allow it to cool, spread the thick mass of crystals on a porous plate, and finally dry the product in a desiccator over lime.

1. *Crystallized Green Chromic Chloride.* Dissolve 50 g. of the impure chloride in 40 c.c. of water, filter, and while keeping cold with a mixture of ice and salt, saturate the solution with gaseous hydrogen chloride. After standing several hours, drain the crystalline paste in a funnel containing a marble around which a thin cord of asbestos is laid. Without washing, dry the crystals one to two days in a desiccator; then stir them up with acetone, which does not dissolve the dry salt, drain the product on a hardened filter, and wash it with acetone until the latter runs through colorless. Yield, 10 to 20 grams.

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[1] Ber. **34**, 1591 (1901).

[2] Z. anorg. Chem. **39**, 296, 320 (1904).

The preparation dissolves in water to an emerald-green solution. If this solution is precipitated with ammonia, and the chromic hydroxide is redissolved in hydrochloric acid while cooling, a violet solution of the other modification of the chloride is obtained. The violet modification is the more stable in solutions that are free from acid.

2. *Crystallized Violet Chromic Chloride.* Dissolve 40 grams of commercial chromic nitrate, $Cr(NO_3)_3 \cdot 9H_2O$ in 40 c.c. of water, add 20 c.c. of concentrated hydrochloric acid, cool with ice and saturate with hydrogen chloride at ice temperature. Collect the precipitate on a double layer of hardened filter paper in a 5 cm. Büchner funnel and wash it with ice-cold concentrated HCl. Dissolve this product in 40 c.c. water, filter if necessary, add 20 c.c. of concentrated HCl and again saturate at the ice temperature with hydrogen chloride. Pour the now almost colorless mother-liquor off and drain the crystal mass on a double layer of hardened filter paper in the Büchner funnel; wash several times with acetone, and lastly with anhydrous ether. Dry the product in a vacuum desiccator over sulphuric acid. The violet chromic chloride can only be kept unchanged when it is completely dry; otherwise it turns green.

CHAPTER VI.

COMPLEX NON-ELECTROLYTES.

In this chapter are brought together a number of different kinds of substances, many of them containing organic radicals, and all of them showing very little, if any, tendency to undergo electrolytic dissociation. The ability of these substances to dissociate otherwise than electrolytically is slight, and most of them can, like many of the pure organic compounds, be distilled without undergoing decomposition. It is characteristic of them, however, that in the presence of water they suffer hydrolysis (saponification) instead of electrolytic dissociation (cf. p. 60). Here, as in the case of organic substances, it is permissible to develop structural formulas, and thus the probable structure of the products of hydrolysis can be derived. For example, it is possible to deduce the structure of certain inorganic acids from the graphic formulas of their chlorides and esters. Cf. Cyanic Acid, p. 113; Oxy-acids of Sulphur, p. 126; Acids of Phosphorus p. 135.

ACID CHLORIDES.

149. Sulphuric Acid Dichloride (Sulphuryl Chloride), SO_2Cl_2, and Sulphuric Acid Monochloride (Chlorosulphonic Acid), $HO.SO_2Cl$.

By the term *acid chloride* is understood a substance which is converted into an oxy-acid when its chlorine atoms are replaced with hydroxyl groups. Sulphuryl chloride, SO_2Cl_2 is the chloride of sulphuric acid:

$$SO_2Cl_2 + 2\ H_2O = SO_2(OH)_2 + 2\ HCl.$$

It is produced by the direct union of sulphur dioxide and chlorine in the sunlight; the combination takes place more readily, however, in the presence of catalyzers such as anhydrous acetic acid, porous charcoal, or, most efficient of all, camphor.

Sulphuric acid monochloride is formed by the partial hydrolysis of sulphuryl chloride, but it can also be prepared from sulphuric acid and phosphorus pentachloride by a reaction which is of very general applicability. Phosphorus pentachloride acts upon substances which contain hydroxyl in such a way that phosphorus oxychloride, hydrogen chloride, and a chloro-substitution product of the original material are formed:

$$R.OH + PCl_5 = RCl + POCl_3 + HCl$$

In certain cases the phosphorus oxychloride itself also acts as a chlorinating agent.

Sulphuric acid monochloride can be prepared in still another way by the direct addition of hydrogen chloride to sulphur trioxide:

$$SO_3 + HCl = HO.SO_2Cl.$$

All acid chlorides have a choking, often very disagreeable odor, and all fume when exposed to moist air. In preparing them, moisture must be excluded with great care.

Sulphuryl Chloride. Connect in series a 500-c.c. distilling flask, a fairly long condenser, and a receiving flask, making all the joints tight with closely fitting cork stoppers. From the receiver lead an escape-tube to the ventilating flue. Through the cork in the neck of the distilling flask pass two tubes, reaching to the bottom of the flask, by means of which sulphur dioxide and chlorine can be introduced separately. Allow the distilling flask to rest in a porcelain dish on a water-bath, which is not heated at the start.

Place 50 g. of camphor in the distilling flask and fill the porcelain dish wth water and a few pieces of ice. Generate sulphur dioxide from 400 g. of copper turnings and 800 g. of concentrated sulphuric acid (or from bisulphite solution, see note, p. 71). Pass the gas first through a sulphuric acid wash bottle and then into the distilling flask, where it is taken up by the camphor, with which it forms a colorless liquid. Then begin to introduce chlorine, which is likewise dried by sulphuric acid (cf. No. 42, p. 69). Regulate the evolution of the two gases so that about equal amounts of each bubble through the washing bottles; an excess of chlorine colors the contents of the distilling flask yellow. Continue the process until this flask is a little more than half filled. Towards the end allow first an excess of chlorine to collect in the flask and then strengthen the stream of sulphur dioxide until this excess is just removed, after which stop the evolution of the gases.

After some time — six to twelve hours — remove the porcelain dish and heat the flask on the water-bath as long as anything distils over; at first a considerable quantity of gas is evolved. If the distillate contains free chlorine remove it by shaking the liquid with mercury (cf. Nos. 51 and 52), and filtering through a perfectly dry asbestos felt in a Gooch crucible. Finally redistil the material from a distilling flask provided with a thermometer and a condenser. Boiling-point, 69.5°.

A mixture of a few drops of sulphuryl chloride and a few c.c. of water reacts slowly with the formation of sulphuric and hydrochloric acids. Larger quantities react, after some time, suddenly and very energetically, with a considerable evolution of heat.

Sulphuric Acid Monochloride.

(a) From Sulphuric Acid and Phosphorus Pentachloride.

The chlorination of sulphuric acid by phosphorus pentachloride takes place according to the equation

$$SO_2(OH)_2 + PCl_5 = SO_2Cl.OH + POCl_3 + HCl.$$

The phosphorus oxychloride formed acts likewise as a chlorinating agent in this case:

$$2H_2SO_4 + POCl_3 = 2SO_2Cl.OH + HPO_3 + HCl.$$

First prepare pure sulphuric acid "monohydrate" by adding fuming sulphuric acid to the ordinary concentrated acid until the specific gravity at exactly 15° is 1.84.

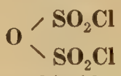
To 200 g. of this acid in a liter flask add 150 g. of phosphorus pentachloride in small portions from a glass spatula. The mixture becomes somewhat heated, and large quantities of hydrogen chloride escape. (The operation should be carried out under the hood, or, better still, out-of-doors.) When all the phosphorus pentachloride has been added, heat the flask on a Babo funnel until the evolution of hydrogen chloride has ceased. Transfer the liquid product to a distilling flask, or a tubulated retort, in which a thermometer is inserted through a ring of asbestos cord (not through a cork). Slip a glass tube, 40 cm. long and 1 cm. in diameter, over the side arm of the distilling flask, or the neck of the retort to serve as an air condenser; it is not necessary to make the joint tight. Distil until the temperature has risen to about 165°. To purify the crude product, redistil it from a fractionating flask with a side arm condenser (Fig. 7, p. 6). Boiling-point, 153°. Yield, 120 to 150 grams.

(b) From Sulphur Trioxide and Hydrogen Chloride. Melt some commercial, 80% fuming sulphuric acid, which can be obtained in small sealed flasks, by placing it for a short time in a warm place. Add 200 g. of this acid to a large, gas-washing flask which has ground glass joints; cool the flask and contents to the room temperature and pass in a vigorous stream of gaseous hydrogen chloride. As soon as the mixture becomes warm, cool it by surrounding the flask with ice. When the hydrogen chloride ceases to be absorbed, transfer the liquid to a distilling flask;

provide an air condenser as in (*a*) and fit a thermometer in the neck of the flask by means of asbestos cord. On distilling the liquid the dissolved hydrogen chloride escapes first. Save the distillate between 150° and 165° and purify it by redistilling. Yield, about 170 g. of sulphuric acid monochloride, boiling-point 153°.

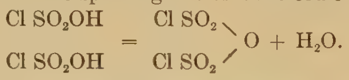
Dependent preparation: Pyrosulphuric Acid Chloride No. 150.

150. Pyrosulphuric Acid Chloride (Disulphuryl Chloride),



$$O\begin{matrix} \diagup SO_2Cl \\ \diagdown SO_2Cl \end{matrix}$$

The action of phosphorus pentachloride on sulphuric acid monochloride results in the formation, not of sulphuric acid dichloride, but of pyrosulphuric acid chloride, with the splitting out of a molecule of water:



$$\begin{matrix} Cl\,SO_2OH \\ Cl\,SO_2OH \end{matrix} = \begin{matrix} Cl\,SO_2 \diagdown \\ Cl\,SO_2 \diagup \end{matrix} O + H_2O.$$

For the purpose of withdrawing the water, however, phosphorus pentoxide serves better than the pentachloride. It is upon this mode of forming the acid chloride that the customary constitutional formula of pyro- or di-sulphuric acid is based.

Introduce 20 g. of phosphorus pentoxide and then 30 g. of sulphuric acid monochloride into a small retort, and close the tubulus with asbestos. Distil slowly without a condenser and catch the distillate in a flask that rests in a bath of cold water.

Redistil the first product from a small flask with a side-arm condenser and with a thermometer made tight with asbestos cord. The liquid boils at 146°. Yield, 20 to 25 grams. Preparations of entirely pure pyrosulphuric acid chloride boil at 152.5–153°.

151. Sulphurous Acid Chloride (Thionyl Chloride) $SOCl_2$.[1]

Provide a liter, round-bottomed flask with a stopper through which a delivery tube and the lower end of a return condenser are inserted, the latter so as to just pass through the stopper and the former so as to reach to the bottom of the flask. Place this apparatus under the hood, and add 500 g. of phosphorus pentachloride (not less) to the flask. Introduce sulphur dioxide (from 200 g. copper and 400 g. concentrated sulphuric acid), purifying it by bubbling it through sulphuric acid and then passing it through a tube filled with crystals of potassium sulphate.

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[1] Another method for preparing thionyl chloride depends on the reaction: $SO_3 + SCl_2 = SO_2 + SOCl_2$.

As soon as all the phosphorus pentachloride is dissolved, stop the flow of gas at once, and subject the resulting mixture of thionylchloride and phosphorus oxychloride to a careful fractional distillation.

Through the cork in the neck of a round-bottomed flask fit a fractionating tower, 35 cm. high, containing a 30-cm. column of coarse glass beads. Connect the side arm of the tower with a condenser and insert a thermometer through a cork placed in the top of the tower. On the first distillation collect four fractions: (1) all that distils up to 82°; (2) between 82° and 92°; (3) between 92° and 105°; (4) between 105° and 115°. The quantity of the fractions varies from 110 to 180 grams. Distil each one of these portions separately in the same apparatus — except that a smaller flask is now used — observing the following plan of procedure: pour fraction (1) into the distilling bulb and place the same flask in position again as receiving vessel. Distil until the temperature reaches 82°, add the contents of receiving flask (2) to the bulb and distil again. Continue to collect in receiver (1) until the temperature again reaches 82°, then exchange this flask for the now empty receiver (2). When the temperature reaches 92° add the contents of receiver (3) and continue to distil into receiver (2) until 92° is again reached; then exchange this flask for receiver (3). At 105° add the contents of receiver (4) and continue to distil into receiver (3) until 105° is once more reached; then change the receivers and collect the distillate in (4) until 115° is reached. It will be found that the middle fractions of the second series of distillations are smaller than in the first series. Repeat the fractionation, whereby the middle fractions become still smaller with a corresponding increase of the end fractions. Finally use only the two end fractions; distil each by itself from the same apparatus after it has been cleaned, and reject a small amount of each both at the beginning and the end of the distillation. About 165 g. of thionyl chloride of boiling-point 77° to 79° and about 180 g. of phosphorus oxychloride of boiling-point 109° to 111° are thus obtained. The yield of thionylchloride amounts to 55–60% of the theoretical, the percentage yield is much lower when smaller quantities are prepared because of the losses incidental to the fractionation: these losses are relatively less in preparing larger quantities. The preparation is not entirely free from phosphorus compounds; it is, however, admirably suited for use as a chlorinating agent in organic chemistry. Its odor is suffocating and offensive.

A few drops of thionyl chloride added to a little water react slowly, — more rapidly on warming, — yielding hydrochloric and sulphurous acids.

To test for the presence of phosphorus, add some nitric acid to the solution just obtained, evaporate to dryness on the water-bath, dissolve the residue in a little water, and test with ammonium molybdate.

Dependent preparation: Symmetrical Ethyl Sulphite, No. 155.

152. Nitrosylsulphuric Acid, $HOSO_2.NO_2$.

Although it contains no chlorine, nitrosylsulphuric acid can be regarded as in the same class with the acid chlorides, because its characteristic atom grouping, $-SO_2.NO_2$, is entirely analogous to that which is present in sulphurylchloride, or in sulphuric acid monochloride. It is, like the two latter compounds, converted by hydrolysis directly into sulphuric acid.

Nitrosylsulphuric acid can be formed by the interaction of sulphur dioxide and nitric acid:

$$SO_2 + HNO_3 = HOSO_2.NO_2$$

or of sulphuric acid and nitrous acid:

$$2H_2SO_4 + N_2O_3 = H_2O + 2HOSO_2.NO_2$$

Because of its formation in the lead chambers of sulphuric acid plants when insufficient water is supplied, this compound has long been known by the name of "chamber crystals" (cf. No. 86).

Place 100 g. of anhydrous nitric acid (cf. No. 34) and 25 g. of anhydrous acetic acid in an Erlenmeyer flask and surround the flask with a freezing mixture. For introducing sulphur dioxide, insert a tube 1 cm. in diameter through the cork. The top of this tube is closed with another cork and just below this stopper a side arm is provided through which the gas is to enter. Whenever the lower end of the tube becomes clogged with crystals, the stopper may be removed for a moment and the obstruction dislodged with a stirring rod (cf. No. 46). Generate the sulphur dioxide from 200 g. of copper turnings and 400 g. of concentrated sulphuric acid (or from bisulphite solution), and pass it through a sulphuric acid wash bottle.

Pass the gas rapidly into the reaction flask, shake the mixture from time to time, and take particular care that it is kept well cooled, since otherwise an energetic, sometimes explosive oxidation may occur according to the equation

$$SO_2 + 2\ HNO_3 = H_2SO_4 + 2\ NO_2.$$

This last reaction is more likely to take place if the nitric acid has not been diluted with acetic acid as recommended above.

Drain the thick crystalline paste, wash it with a little cold, glacial acetic acid, then freely with carbon tetrachloride, and dry the product in a vacuum desiccator over sulphuric acid. The crystals obtained in this manner can be preserved in a well-stoppered flask for a long time unchanged. Yield, about 80 to 90 g.

ESTERS.

Esters are derived from acids by the replacement of the acid hydrogen atoms by hydrocarbon radicals; they are often called "etherial salts," but are to be distinguished from ordinary salts by their inability to dissociate electrolytically.

$$\underset{\text{Nitric Acid.}}{HNO_3} \qquad \underset{\text{Methyl nitrate (methylester of nitric acid).}}{CH_3NO_3}$$

Of the methods of forming such substances the following three will be considered here:

1. From an acid and an alcohol with elimination of water:

$$\underset{\text{Ethyl Alcohol}}{C_2H_5OH} + HNO_3 = H_2O + \underset{\text{Ethyl Nitrate}}{C_2H_5NO_3} \qquad \text{(No. 153)}$$

2. From an acid chloride and an alcohol with elimination of hydrogen chloride:

$$\underset{\text{Thionyl Chloride}}{SOCl_2} + \underset{\text{Ethyl Alcohol}}{2\ C_2H_5OH} = 2\ HCl + \underset{\text{Diethyl Sulphite}}{SO_3(C_2H_5)_2} \quad \text{(No. 155)}$$

3. From the silver salt of an acid and an alkyl halide:

$$\underset{\text{Silver Sulphite}}{Ag_2SO_3} + \underset{\text{Ethyl Iodide}}{2\ C_2H_5I} = 2\ AgI + \underset{\text{Diethyl Sulphite}}{SO_3(C_2H_5)_2} \quad \text{(No. 156)}$$

The first method of formation is reversible; the opposed reaction, by which the ester is broken down, is termed *saponification* and is in its nature quite identical with the hydrolysis of salts. Since the saponification of esters takes place much more slowly than the hydrolysis of salts, it is admirably adapted for the study of reaction velocities (see text books on Physical Chemistry). Inasmuch as the two opposed reactions — esterification and saponification — often lead to an equilibrium in which all four of the reacting substances are present in finite determinable concentrations, this so-called "ester equilibrium" is used with great success in demonstrating the law of mass action. This law requires that at a constant temperature the relation expressed in the following equation shall hold true:

$$\frac{[\text{Ester}] \cdot [\text{Water}]}{[\text{Acid}] \cdot [\text{Alcohol}]} = K.$$

It is evident from this equation that to obtain a favorable yield of ester the concentration of the water should be kept as low as possible. This can be accomplished in practice by adding concentrated sulphuric acid to the reaction mixture. On the other hand, saponification is favored by the removal of the acid, and this can be brought about by the addition of a base.

153. Ethyl Nitrate, $C_2H_5ONO_2$.

Ethyl nitrate is formed from nitric acid and ethyl alcohol according to Method 1 described above. Since, however, the nitric acid may also act as an oxidizing agent upon the alcohol, and since, moreover, the oxidation is so vigorously catalyzed by the lower oxides of nitrogen that the mixture sometimes decomposes explosively, the expedient is adopted of adding urea, which removes the reduction products of nitric acid. Urea reacts with nitrous acid according to the equation

$$CO(NH_2)_2 + 2\ HNO_2 = CO_2 + 2\ N_2 + 3\ H_2O.$$

Place in a 150-c.c. distilling flask 38 g. of absolute alcohol, 6 g. of urea, and 60 g. of concentrated nitric acid (sp. gr. 1.4) which has previously been boiled with 0.5 g. of urea. Distil the mixture on the water-bath, and when about one-third has passed over, add slowly from a dropping funnel a further mixture of 100 g. of concentrated nitric acid (which has likewise been boiled with a gram of urea and subsequently cooled to the room temperature) and 75 g. of absolute alcohol. Continue the distillation until nothing more passes over. Purify the ester from acid and alcohol by shaking it three times with water in a separatory funnel, using a double volume of water for the first shaking. Free the layer of ester as completely as possible from drops of water by pouring it into a dry flask, and let it dry by standing several hours in contact with granular calcium chloride. Finally, distil the product with the bulb of the flask immersed in a water-bath. Yield, about 40 g. of a colorless liquid which boils sharply at 87°. On setting fire to a few drops of the ethyl nitrate, it burns with a pale flame.

By allowing larger amounts of the above mixture to drop into the reaction flask, the ester may be prepared conveniently in considerable quantity.

154. Amyl Nitrite, $C_5H_{11}.ONO$, and Methyl Nitrite, $CH_3.ONO$.

Amyl nitrite is easily formed by the action of nitrous acid on amyl alcohol. Since neither amyl nitrite nor amyl alcohol are miscible with water, the progress of this esterification is not retarded by the presence of water.

To 50 g. of amyl alcohol and 300 g. of cold, 20% sulphuric acid in a 750-c.c. flask add 60 g. of sodium nitrite in small portions while shaking the flask continuously and cooling under the water tap. Wait, before adding each fresh portion, until the reaction from the previous addition is ended and the yellowish-red vapors have disappeared from the flask. About 30 minutes is required for this operation. After waiting an hour longer, separate the layers in a separatory funnel, wash the oily layer twice by giving it a rotary motion with water (but do not shake it, as an emulsion then forms which will separate into layers only on long standing), free the liquid from drops of water, and let it dry by standing overnight with lumps of fused calcium chloride. Distil the ester from a fractionating flask with a side-arm condenser. Boiling-point, 97°. Yield, about 60 grams.

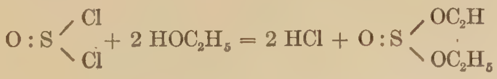
Methyl Nitrite.

Methyl alcohol and amyl nitrite interact readily with the formation of methyl nitrite and amyl alcohol. Amyl nitrite is much used in organic chemistry as a reagent in preparing nitroso and diazo compounds.

Mix amyl nitrite with about one-third its weight of methyl alcohol. After a short time, or sooner on warming gently, methyl nitrite (boiling-point, − 12°) begins to escape as a gas. By using 25 g. of amyl nitrite and 7 g. of methyl alcohol, several cylinders full of gas may be obtained. When set on fire it burns with a pale flame.

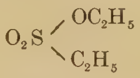
155. Symmetrical Diethyl Sulphite, $SO(OC_2H_5)_2$.

There are two isomeric substances of the composition $(C_2H_5)_2SO_3$, both of which are to be regarded as esters of sulphurous acid. One of them is produced by the action of thionyl chloride on ethyl alcohol, and upon being saponified it yields sulphurous acid and alcohol; the other can be formed from a sulphite and a halogen alkyl, or by the esterification of ethyl sulphonic acid, $C_2H_5SO_2.OH$. Since it is only possible for thionyl chloride to have the structural formula $O:SCl_2$, the ester formed from it must have the corresponding symmetrical structure



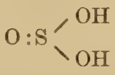
$$O:S\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + 2\,HOC_2H_5 = 2\,HCl + O:S\begin{matrix}\diagup OC_2H\\ \diagdown OC_2H_5\end{matrix}$$

On the other hand, in ethyl sulphonic acid, since this can be formed by the oxidation of ethyl mercaptan, $C_2H_5.SH$, it must be true that the ethyl is bound directly to the sulphur atom, and that therefore the compound has the structural formula $C_2H_5.SO_2.OH$, while its ester has the corresponding unsymmetrical structure



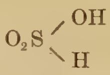
$$O_2S\genfrac{}{}{0pt}{}{\diagup OC_2H_5}{\diagdown C_2H_5}$$

As regards the sulphites and free sulphurous acid there are, therefore, two possible formulas. The fact that solid sulphites react with halogen alkyls to form unsymmetrical esters suggests that the sulphites have an unsymmetrical structure. There is no positive proof as to whether the constitution of free sulphurous acid is represented by the formula



$$O:S\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown OH}$$

or by the formula



$$O_2S\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown H}$$

It is perfectly possible that both forms of the acid may exist together in a state of mobile equilibrium (cf. Cyanic Acid, No. 73). Such a condition is known as *tautomerism* or *dynamic isomerism* (cf. A. Findlay, The Phase Rule, p. 193.)

Insert a dropping funnel through a cork in the mouth of a 75-c.c. flask with side-arm condenser (Fig. 7, p. 6), so that the stem of the funnel reaches just to the bulb of the flask. Place 40 g. of thionyl chloride (one-third mol) in the bulb and surround it with a mixture of ice and salt. Then allow 31 g. of alcohol (which has been dehydrated by standing two hours over a large quantity of quicklime and then distilled), to drop into the flask. The alcohol should be added very slowly at first, as the reaction is violent and considerable heat is evolved. The operation requires thirty to forty-five minutes. Finally let the liquid become warmed to room temperature, whereby hydrogen chloride escapes freely (Hood), exchange the dropping funnel for a thermometer, and distil. At first, in addition to hydrogen chloride, a little alcohol passes over, then about 38 g. of ethyl sulphite distils between 130° and 160°. Redistil the crude product after cleaning and drying the apparatus. About 35 grams of the pure ester are obtained, boiling at 158° to 158.5°.

The ester is a colorless oil of an agreeable odor, and is somewhat more viscous than water. It is not decomposed by water even on boiling, but when treated with caustic soda, it is saponified with the formation of ethyl alcohol and sodium sulphite. Warm a few drops of the ester with 2 c.c. of caustic soda and a few drops of alcohol, drive off the latter by boiling a short time, cool, and acidify the solution with dilute sulphuric acid. Sulphur dioxide escapes and can be recognized by its odor.

Saponify a second portion in like manner by adding barium hydroxide together with a few drops of alcohol; boil off the alcohol and acidify the cooled solution with nitric acid. At first no change is noticed, but on boiling a cloudiness appears which is caused by the precipitation of barium sulphate.

156. Unsymmetrical Diethyl Sulphite, $C_2H_5.SO_2.OC_2H_5$.

To prepare silver sulphite, which is to serve as the starting material for this preparation, pass a stream of sulphur dioxide into a solution of 150 g. silver nitrate in 500 c.c. of water. Keep the mixture cooled with water, and continue the process until a small filtered portion of the solution no longer gives a precipitate with hydrochloric acid. Drain the precipitated silver sulphite immediately and wash it successively with water, alcohol, and ether; then dry it over sulphuric acid in a vacuum desiccator.

The next day place the silver sulphite and 1.1 times its weight of ethyl iodide in a flask, provided with a return condenser, and allow the mixture to stand overnight. The top of the condenser should be closed with a calcium chloride tube to exclude moisture; the outer jacket should be filled with water, but a constant flow need not be maintained. After 24 hours, add 150 to 200 c.c. of thoroughly dry ether (which has stood for several days in contact with sodium wire), and boil the mixture six hours on the water-bath with return condensation, still protecting from atmospheric moisture with the calcium chloride tube. Filter the liquid from the silver iodide[1] and wash the latter with ether; distil the ether from the filtrate, using a tower containing glass beads. Then fractionate the liquid in a smaller flask, using a tower with a column of glass beads 13 cm. high and 1.5 cm. wide (cf. No. 151). Reject the first runnings up to 100°; collect two fractions, first from 100° to 200°, and second at above 200°, and refractionate these portions repeatedly according to the process described in No. 151. The pure, unsymmetrical diethyl sulphite boils sharply at 214°–215° (760 mm.). Yield, 12 to 18 grams of a colorless oil, quite similar to the symmetrical ester. It is immiscible with water, but is slowly saponified by it. Alkalies in alcoholic solution cause saponification to take place more quickly.

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[1] Recover the silver from the silver iodide residue by reducing it with a warm solution of sodium hydroxide and dextrose, and then melting the silver powder obtained with twice its weight of sodium carbonate.

$$C_2H_5SO_2.OC_2H_5 + H_2O = C_2H_5SO_2.OH + C_2H_5OH.$$

Allow four drops of the ester to stand a few minutes with an equal amount of alcoholic potassium hydroxide solution. The mixture becomes warm and a solid separates. On acidifying with sulphuric acid and boiling, no sulphur dioxide is evolved. This behavior distinguishes the unsymmetrical from the symmetrical ester.

157. Triethyl Phosphate, $PO(OC_2H_5)_3$.

Add 14 g. of freshly-cut sodium to 150 c.c. of absolute alcohol, and after the reaction moderates, heat the mixture on the water-bath with a return condenser until all the metal has dissolved. Cool the sodium ethylate solution with ice and salt, then add, drop by drop, 31 g. of phosphorus oxychloride (No. 46); each drop reacts energetically and much heat is evolved. After some time, drain the solution on a Büchner funnel from the precipitated sodium chloride and rinse the residue with a little anhydrous ether. The sodium chloride is so finely divided, however, that it cannot be removed completely. Distil the alcohol and ether from the filtrate, placing the bulb of the flask on the water-bath and wrapping the upper part and neck with a towel. Pour the residual liquid through a smaller filter — it still comes through somewhat cloudy — and distil it from a fractionating flask with a side-arm condenser (Fig. 7, p. 6). Collect the first runnings up to 110° and the main portion above 110°; some sodium chloride is left in the flask. Fractionate the distillate which comes over above 110° twice more from the same distilling flask, after cleaning it; a pure product is readily obtained which boils sharply at 217°–218°. Yield, 20 to 25 g. Triethyl phosphate is a colorless oil having a typical etherial odor. It is miscible with water and is saponified by it to diethyl phosphoric acid.

158. Tetraethyl Silicate, $Si(OC_2H_5)_4$.

To about 20 g. of silicon tetrachloride (No. 51) in a small flask allow 1.1 times its weight of absolute alcohol to flow slowly from a dropping funnel. The alcohol must have been boiled with quicklime for several hours immediately beforehand and then distilled out of contact with moisture. During the operation hydrogen chloride escapes in quantity; it is not necessary to cool the mixture since it becomes warmed but little.

Purify the crude product by distilling it from a small round-bottomed flask and through a fractionating tower containing a 13 cm. column of glass beads. Use an air condenser consisting of a tube 40 cm. long and 1 to 1.5 cm. in diameter, which is loosely slipped over the side-arm of the tower; a cork connection is unnecessary. Collect two fractions during the first distillation — the first one, which is large in quantity, between 160° and 175°, and the second, which is smaller, between 175° and 185°. On the second fractionation, collect a small amount of first runnings and then portions from 167° to 170° and from 170° to 180°, respectively. Finally, after cleaning and drying the apparatus, distil the fraction boiling between 167° and 170° again, whereby nearly all goes over between 168° and 169°. Yield, 13–15 g.

Small amounts of higher boiling by-products are formed and consist of esters of metasilicic and polysilicic acids.

Tetraethyl silicate is a colorless liquid having a typical etherial odor; it is immiscible with water, but it dissolves in dilute alcohol and gradually undergoes hydrolysis in that solution.

METAL-ORGANIC COMPOUNDS.

The metal in the metal-organic compounds is bound directly to hydrocarbon radicals or to carbon monoxide: $Zn(C_2H_5)_2$, zinc ethyl (No. 159); $Pb(C_6H_5)_4$, lead tetraphenyl (No. 160); $Ni(CO)_4$, nickel carbonyl (No. 161). The low boiling-points of these compounds, which would scarcely lead one to suspect the presence of a metal, permit in most cases a ready determination of the vapor density and thus of the molecular weight. In this respect, as in fact in almost their entire chemical behavior (e.g. the ready solubility in organic solvents), these compounds show themselves to be closely related to the purely organic compounds. It is, therefore, not surprising that the theory which has found its most specific application, as well as its greatest success, in the field of organic chemistry — namely the valence theory in its original form — should have originated in the discovery of these very metal-organic compounds. It was not until Frankland (1853) had recognized that the saturation capacity of the metals in these compounds could be measured by the number of univalent organic radicals which are joined directly to the metal atom that this combining capacity began to be regarded as a fundamental property of the metals — as well as of all other elements — which governs their behavior in all of their compounds.

159. Zinc Ethyl. $Zn(C_2H_5)_2$.

Zinc and ethyl iodide when heated together combine to form ethyl-zinc iodide:

$$Zn + I.C_2H_5 = C_2H_5.Zn.I,$$

and upon stronger heating the ethyl-zinc iodide is transformed into zinc ethyl and zinc iodide:

$$2\ C_2H_5.Zn.I = Zn(C_2H_5)_2 + ZnI_2.$$

The formation of ethyl-zinc iodide, which does not always prove successful when zinc alone is used, can be accomplished with certainty if instead of zinc an intimate mixture of zinc and copper (zinc-copper couple) is employed.

Zinc ethyl takes fire spontaneously when it comes in contact with the air, and it is, therefore, a dangerous substance. Above all, care should be taken to prevent its coming in contact with the skin, for the burns produced heal only with difficulty. With suitable precautions, however, it is possible to work quite safely with zinc ethyl; it can, for example, be transferred from one vessel to another without danger if a plentiful supply of carbon dioxide is allowed to flow over the openings as well as to fill the interiors of the vessels.

Place an intimate mixture of 100 g. zinc dust and 12 g. of finely powdered and sifted copper oxide in a glass tube of 2.5 cm. diameter. Lay the tube in a shallow trough of asbestos paper over a row burner and pass into it a stream of dry hydrogen. After proving the purity of the hydrogen, heat the mixture gently, allowing the flames to only just touch the asbestos. During the reduction the mass becomes lighter in color and swells up to a considerable extent; on this account the tube ought not to be more than half filled with the mixture at the outset. At the end of half an hour, if no more water vapor escapes from the tube, extinguish the flame and allow the material to cool in an atmosphere of hydrogen.

Place 100 g. of this zinc-copper mixture and 100 g. of ethyl iodide in a 200 to 300 c.c. Erlenmeyer flask and attach a return condenser. Heat the mixture on the water-bath until a thick, grayish mass is formed and no more ethyl iodide condenses and drips back (20 to 30 minutes). Then remove the condenser and place in the mouth of the flask a cork which is already fitted with a gas delivery tube to reach into the lower third of the flask and with another tube leading to a condenser. Place at the lower end of the condenser, to serve as a receiving vessel, a 100-cc. distilling flask with a side-arm condenser (Fig. 7, p. 6). All the joints should be made air-tight with corks. After filling the entire apparatus with carbon dioxide, heat the Erlenmeyer flask to 180 to 220° in an oil-bath, whereupon zinc ethyl distils over.

Some time after the distillation is finished, disconnect the receiving vessel and stopper it immediately with a cork, already made ready, which carries a thermometer and a carbon dioxide delivery tube. Keeping a plentiful supply of carbon dioxide flowing through the apparatus, redistil the liquid. Catch the first runnings of zinc ethyl mixed with ethyl iodide in a test-tube filled with carbon dioxide. At 110° interrupt the distillation, and replace the test-tube with a thick-walled tube drawn out near its upper end preparatory to being sealed off. Fill this tube likewise with carbon dioxide and distil over all the liquid, heating the entire distilling flask at the last by fanning it with the flame. Then seal the tube immediately with the blast lamp. Carefully avoid any access of air at this or any previous part of the operation, since this would cause immediate ignition of the zinc ethyl. Boiling-point, 118°. Yield, about 30 g.

160. Lead Tetraphenyl, $Pb(C_6H_5)_4$, by Means of Grignard's Reagent; Diphenyl Lead Iodide, $Pb(C_6H_5)_2I_2$.

The action of metallic magnesium upon etherial solutions of alkyl halides results, as was discovered by Grignard, in the formation of compounds in which the alkyl radical is bound directly to the magnesium:

$$C_6H_5Br + Mg = C_6H_5MgBr.$$

The compounds formed are soluble in ether, and themselves contain ether; their etherial solutions, which constitute the so-called *"Grignard's reagent,"* can be employed for transferring alkyl groups to different metals as well as to organic radicals of the most varied types.

$$2\,PbCl_2 + 4\,C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 2\,MgCl_2 + 2\,MgBr_2.$$

Lead Tetraphenyl. Place 70 g. of perfectly dry ether, which has stood several days in contact with sodium wire, and 25 g. of brombenzene in a small flask. Add 3.7 g. of magnesium ribbon which has been scraped clean with a knife, close the flask with a calcium chloride tube and allow it to stand 24 hours in a dish of water. When all the magnesium has dissolved, add, while shaking, 24 g. of dry powdered lead chloride in small portions, and allow the mixture to stand for two days with occasional shaking. Then add this mixture, a little at a time, to 200 c.c. of water and acidify faintly with dilute hydrochloric acid. Collect the precipitate (which is colored dark by precipitated lead) on a suction filter, wash it with water, and dry it in the hot closet. The mass becomes lighter colored on drying and weighs about 15 g. Boil the material with two successive portions of 100 c.c. each of benzene, using a reflux condenser, and concentrate the combined filtrates in a distilling apparatus[1] to about 75 c.c. Colorless, glistening prisms, melting-point 222° to 224°, crystallize from the liquid. Yield, 8 to 9 g.

Further concentration of the mother-liquid furnishes but little additional product.

Diphenyl-lead-iodide. $(C_6H_5)_2PbI_2$.

Two of the phenyl groups in lead tetraphenyl can be replaced with hydroxyl groups, or with acid radicals:

$$Pb(C_6H_5)_4 + 2\,I_2 = (C_6H_5)_2PbI_2 + 2\,C_6H_5I.$$

Dissolve 3 g. of lead tetraphenyl by warming it with 60 g. of chloroform. After cooling add carefully a cold solution of 3 g. iodine in a little carbon disulphide until the color of the iodine just fails to disappear. Allow the yellow solution to evaporate in a warm place; extract the residue first with 10 c.c. and then with 5 cc. of carbon disulphide; concentrate[2] the filtered extract to a volume of between 5 and 10 c.c.; and allow it to crystallize, after the addition of 2 to 3 c.c. of absolute alcohol. Drain the deep lemon-yellow crystals, wash them with a little alcohol, and dry them at a gentle heat. The product melts with decomposition[1] at 105 to 107°. The yield is not quite quantitative, as some lead iodide is always formed.

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[1] Benzene vapors are inflammable and burn with a smoky flame.

[2] Small quantities of carbon bisulphide and other inflammable liquids can be evaporated over a free flame in an open vessel if the vapors are drawn rapidly away through a tube connected with the suction pump. The tube should be inserted about one-third the way into the beaker or flask.

161. Nickel Carbonyl,[2] $Ni(CO)_4$.

When carbon monoxide is conducted over very finely divided nickel, four molecules of the gas combine below 100° with one atom of nickel to form nickel carbonyl (boiling-point, 43°). At higher temperatures this compound dissociates and the nickel separates in the form of a dust, or deposits as a mirror on the walls of the vessel. In making the preparation a careful maintenance of the proper temperature and a state of very fine subdivision of the metal are important; nickel is obtained in the desired condition by reducing nickel oxalate in a current of hydrogen.

Treat a hot solution of nickel sulphate with oxalic acid, then add ammonia, but without entirely neutralizing the solution. The precipitation of nickel oxalate in this way is not quite quantitative, but the product can be washed readily by decanting with hot water. By draining the precipitate and drying it in the hot closet, a light-green, loose powder is obtained.

The carbon monoxide may be prepared by allowing 30 g. concentrated formic acid to slowly drop from a dropping funnel into a distilling flask containing 100 g. concentrated H_2SO_4 at about 100°, and passing the gas through two wash-bottles containing concentrated sodium hydroxide solution. Collect the carbon monoxide in a gasometer.

The reduction of the nickel oxalate and the synthesis of the nickel carbonyl may be accomplished in the same apparatus. Connect two sulphuric acid wash bottles in series at one end of a combustion tube about 26 cm. long, and beyond them place a three-way cock through which either hydrogen from a Kipp generator or carbon monoxide from the gasometer may enter. The carbon monoxide, before entering the tube, must be further purified from traces of carbon dioxide by passing through two bottles containing caustic soda solution. Place an asbestos heating box[1] (cf. Fig. 4, p. 3) around the combustion tube and insert a thermometer into the chamber. Heat the tube by means of a Bunsen burner with a flame spreader, but do not place the flame immediately under the lower opening of the box. Clamp the combustion tube so that it slants downward a little and provide an extra burner to expel any water which may condense inside the tube.

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[1] Diphenyl is formed: $(C_6H_5)_2PbI_2 = PbI_2 + C_6H_5.C_6H_5$. The same decomposition takes place slowly even in a solution of diphenyl-lead-iodide. The diphenyl is easily recognized by its characteristic odor.

[2] Mond, Langer, and Quincke, Chem. News, **62**, 97 (1890).

Place 5 to 7 g. of nickel oxalate in the tube between two loose plugs of asbestos, replace the air completely with hydrogen, and heat the charge to 300° in a current of hydrogen until it has become black and no more water vapor escapes. Avoid a higher temperature, as the nickel would then lose its condition of fine subdivision. Then allow the temperature to sink to between 80° and 100°, and replace the hydrogen by means of a current of air-free carbon monoxide (the wash bottles and connections should be filled with carbon monoxide before beginning the operation). Test the escaping gases for nickel carbonyl as follows:

1. Insert into the end of the combustion tube a cork carrying a tube drawn out to a capillary jet; set fire to the escaping gas; it burns with a brilliantly luminous flame from which metallic nickel is deposited upon a cold piece of porcelain in a form resembling soot.

2. Connect the combustion tube by means of rubber tubing with a carefully cleaned glass tube, and heat the latter gently with a Bunsen burner; a mirror of nickel is deposited in the heated part. If the tube is heated to redness the nickel is then precipitated in the form of a powder.

If the procedure above outlined is carried out on a larger scale the nickel carbonyl vapor issuing from the apparatus may be condensed by passing it into a vessel surrounded by a freezing mixture. Nickel carbonyl is a colorless liquid which boils at 43° under 751 mm. pressure, and solidifies at $-25°$ to a mass of needle-shaped crystals.

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[1] The openings in the cover of the heating box should be covered with discs of asbestos to avoid drafts.

CHAPTER VII.

PREPARATION OF COMPOUNDS OF THE RARE ELEMENTS FROM THEIR MINERALS.

In this chapter methods are described for preparing compounds of some of the rarer elements. It has seemed advisable to devote to these elements a special chapter in which the chief stress is laid upon the methods of working up the natural raw materials, and upon the characterization of the individual elements by the aid of their compounds, rather than upon a classification of the compounds according to types.

162. Lithium Carbonate from Lepidolite, Petalite, or Spodumene; Spectroscopic Tests for Rubidium and Other Metals.

Mix 100 g. of the finely powdered mineral intimately with 100 g. of ammonium chloride and 200 g. of finely powdered calcium carbonate; heat the mixture in a clay crucible, at first gently for half an hour, and then strongly for an hour in the furnace. Break up the sintered mass and extract it about ten times by boiling with 750 to 1000 c.c. of water in a large evaporating dish. Pour off the solution each time through a plaited filter and begin at once to concentrate the filtrate in a second evaporating dish. After the entire filtrate has been reduced to about one liter, make it alkaline with ammonia and add ammonium carbonate until a little of the liquid when filtered gives no further precipitation with the reagent. Drain the solution, on a suction filter, from the precipitated calcium carbonate, and, as the latter contains some lithium carbonate, dissolve it in acetic acid, dilute to about 1.5 liters and precipitate this solution cold with oxalic acid. After the precipitate has settled, filter and add the filtrate to the main solution of the lithium salt. Evaporate the entire solution to dryness, and drive off the ammonium salts from the residue by gentle ignition. Then moisten the substance with concentrated hydrochloric acid and dissolve it in a little hot water; again evaporate the solution to dryness, and dehydrate the residue completely by heating to about 160°. Extract the residue with absolute alcohol either in a Soxhlet apparatus or in a simple flask with a return condenser. In the latter case, extract eight times and distil each of the alcoholic solutions poured from the insoluble residue, using the alcohol, thus recovered, for the next extraction. Finally, after all of the alcohol has been distilled from the extract, dissolve the salt in a little water and precipitate lithium carbonate by adding ammonium carbonate and a little ammonia. From lepidolite 1 to 3 g. of pure lithium carbonate should be obtained, from petalite a little more, and from spodumene about twice as much. Test the purity of the preparation by means of the spectroscope.

The insoluble salt left by the alcoholic extraction contains rubidium, besides other of the alkali metals. Dissolve it in water, treat the solution with about 1 c.c. of 10% chlorplatinic acid solution, and allow it to stand over night. Next morning filter off the insoluble chlorplatinates and ignite them in a Rose crucible in a current of hydrogen. Dissolve the residue in a little water and test it with the spectroscope for rubidium.

Spectroscopic Analysis.

The scale of the spectroscope, which is usually graduated arbitrarily, must first be standardized according to the wave lengths of light. After the apparatus is properly set up, make the sodium line fall upon a certain division of the scale; or, in case the scale telescope is not movable, observe the position of this line as accurately as possible. Then note the position of the following lines:

	Wave Length		*Wave Length*
K_α red	768 × 10^{-6} mm.	Sr_δ blue	461 × 10^{-6} mm.
Li_α red	671 "	H_α red	656 "
Na yellow	589 "	H_β blue	486 "
Tl green	535 "	H_γ violet	434 "

The hydrogen lines are very sharp and easy to observe; ready prepared tubes filled with hydrogen under diminished pressure can be used, and are to be excited by means of an induction coil. Plot the scale readings as abscissas and the corresponding wave lengths as ordinates, and connect the separate points by a smooth curve. One millimeter on the plot may be taken to represent one scale division, and one-half millimeter on the other axis to represent one unit of wave length. From this curve the wave length may be read that corresponds to each division on the scale.

If the lithium preparation is pure it shows only the line 671, and eventually the weaker line at 610, when subjected to the spectroscopic test. If it still contains calcium a red line appears at 616, and green bands at about 500. Rubidium is recognized by red lines at 795 and 780; caesium by the yellowish-red lines 622, 601, 584, and the blue lines 459 and 456.

163. Beryllium Hydroxide from Beryl.

Beryl is essentially a beryllium aluminum silicate, $3\,BeO.Al_2O_3.6\,SiO_2$, and is most readily decomposed by treatment with acid ammonium fluoride, whereby silicon fluoride escapes as a gas, aluminum goes into the difficultly soluble aluminum fluoride, and beryllium into the soluble beryllium fluoride. The beryllium fluoride is transformed into the sulphate, and the latter is dissolved in water and freed from traces of aluminum by means of concentrated ammonium carbonate solution. Beryllium remains in the solution as a double compound with ammonium carbonate. The small amount of iron present is precipitated by adding ammonium sulphide, and the beryllium is finally thrown from the filtrate in the form of hydroxide.

Treat 50 g. of finely powdered beryl in a large platinum dish with 200 g. of neutral ammonium fluoride and 300 g. of concentrated hydrofluoric acid, and heat the mixture under the hood on a Babo funnel until thick vapors escape freely. Continue the heating and gradually increase the temperature until the escape of vapors practically ceases, allow the porous mass to cool, rub it to a powder with a platinum spatula or a wooden stick, and heat again until nothing more is vaporized. Boil the residue, which amounts to about 37 g., five times with water, allowing the sediment to settle and decanting the clear liquid through a plaited filter after each extraction. About 15 g. of aluminum fluoride remain undissolved after this treatment. Evaporate the filtrate in a platinum dish, heat the residue with 30 g. of concentrated sulphuric acid until thick fumes of sulphur trioxide escape, and dissolve the dry sulphate in 100 to 200 c.c. of water. Stir this solution slowly into a cold solution of 150 g. of ammonium carbonate in 600 c.c. of water, whereby only a slight clouding should occur. Then dilute with an equal volume of boiling water and add 2 to 3 c.c. of ammonium sulphide, whereby any iron present — which is usually but little — gives a voluminous precipitate of iron sulphide. Filter through a large plaited filter, the point of which is reinforced by linen cloth folded under it. Wash the precipitate with hot water containing a little ammonium sulphide, and concentrate the filtrate to one-half. The beryllium precipitates as beryllium hydroxide during the evaporation. Collect the precipitate on a filter and boil down the solution still further, thus obtaining the little beryllium which is left as a less pure product than the first. Wash the hydroxide with water and dry it at a gentle heat. Yield, about 13 g. By igniting, 5 to 6 g. of beryllium oxide could be obtained as a loose white powder, but for use in the following preparation the hydroxide should be taken.

If a large platinum dish is not available for the above work, a sheet-iron crucible can be used.

164. Basic Beryllium Acetate, $Be_4O(CH_3CO_2)_6$.

Beryllium hydroxide and acetic acid form a stable and very remarkable compound of the above composition. It melts undecomposed sharply at 289.5, and boils, also without decomposition, at 342 to 343°. This acetate can be used to purify beryllium preparations from all other metals, and it can be obtained of such a definite composition and in such a high degree of purity that it has been used for determining the atomic weight of beryllium.[1]

Dissolve the beryllium hydroxide obtained in No. 163 by warming it with dilute acetic acid. Evaporate the solution on the water bath and dissolve the gummy residue in about 200 c.c. of glacial acetic acid (Hood). Heat the mixture (still under the hood) and filter the solution at the boiling temperature; the salt crystallizes on cooling in beautiful colorless needles or octahedra. Concentrate the mother-liquor to one-fourth, in order to obtain the small remainder of the salt, and dry the entire product in the steam closet.

Determine the melting-point. Boil a sample of the preparation in a test-tube; the vapors condense on the cooler upper walls to form a white crust, and almost no residue remains in the bottom of the tube. The salt is insoluble in cold water but is decomposed by hot water. It is slightly soluble in alcohol, less so in ether, but dissolves readily in chloroform.

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[1] C. L. Parsons: J. Am. Chem. Soc. **27**, 721 (1904).

165. Columbium and Tantalum Compounds from Columbite.

Columbium and tantalum, the most important elements in columbite and tantalite, are separated from one another by crystallizing their potassium double fluorides. Potassium tantalum heptafluoride, $K_2[TaF_7]$, is but sparingly soluble, and crystallizes from a dilute solution, whereas potassium columbium oxyfluoride, $K_2[CbOF_5]$, separates only from a concentrated solution. This classic method was originated by Marignac in 1866, and is still used almost exclusively; in this way the first perfect separation of the two elements was obtained.

Concerning the history of these elements, it is of interest to note that Hatchett, in 1801, first obtained from American columbite a peculiar acid which ten years later was shown by the researches of Wollaston to be identical with a similar acid obtained by Eckeberg in 1802 from Swedish minerals and named by him tantalic acid. The influence of Berzelius led to the adoption of the name tantalum for the element. By more careful researches dating from 1844, H. Rose found in columbite a new element, columbium, and of this he was the first to obtain pure compounds. He believed for a time that a third element, which he named pelopium, was also present. Matters were further complicated by the assumption by various investigators of other elements in this group, and it remained for the work of Marignac to show that all of the minerals worked with contained both columbium and tantalum in varying proportions, and that the preparations studied up to that time were, for the most part, mixtures.

Heat 100 g. of potassium bisulphate gently in a platinum dish until it has reached a state of quiet fusion; allow the mass to just solidify, and distribute 25 g. of finely powdered columbite over its surface. Heat again with slowly rising temperature until finally a clear melt is obtained. Allow the mass to cool, or chill it by placing in cold water; break up the solid mass and allow it to stand in water over night. Next morning pour off the clear solution, and boil out the residue several times with water containing a little hydrochloric acid. Finally collect the residue on a plaited filter, wash it with hot water containing hydrochloric acid, and dry it in the hot closet.

To purify this product completely, fuse it again with potassium bisulphate exactly as before and wash the residue very thoroughly with the dilute acid. Yield, 25 g. of a powder consisting of the oxides of tantalum and columbium, and containing 30 to 50% of water; the powder is usually entirely free from iron.

Determine the actual amount of the oxides present by igniting 0.6 g. of the powder in a platinum crucible to constant weight. For each gram of the anhydrous oxides, 2.5 g. of concentrated hydrofluoric acid and 0.5 g. of potassium carbonate are to be used. The hydrofluoric acid must be pure and above all free from fluosilicic acid. Test for the presence of the latter with potassium salt solution in a platinum crucible.

First dissolve the oxides in the hydrofluoric acid, and pour the solution cold through a plaited filter placed in a funnel which has been coated with paraffin. Allow the filtrate to run into a platinum dish containing a filtered solution of the required amount of potassium carbonate. Dissolve the resulting precipitate by boiling and adding sufficient water, then evaporate the solution until crystals begin to deposit. On cooling, fine needles of potassium tantalum fluoride are obtained. After twelve hours collect the crystals on a plaited filter in a paraffined funnel and wash them with cold water. On further evaporation of the filtrate the remainder of this salt (which is but very little) can be obtained.

Finally, concentrate the solution to a much smaller volume until, instead of the fine needle-like crystals, larger thin plates of potassium columbium oxyfluoride are obtained. Several further crops of these crystals should be obtained from the mother-liquor.

Recrystallize both of the salts from water containing some hydrofluoric acid. Yield, usually about 1.5 g. $K_2[TaF_7]$ and 30 g. $K_2[CbOF_5]$; but the relative quantities of the two salts vary according to the composition of the original material.

166. Molybdenum Compounds from Molybdenite.

Molybdenum occurs in nature to some extent in the form of molybdates (wulfenite, $PbMoO_4$, and powellite, $CaMoO_4$), but the most important ore is the sulphide (molybdenite, MoS_2).

(*a*) *Ammonium Molybdate*, $5(NH_4)_2MoO_4 \cdot 7MoO_3 \cdot 7H_2O$.

Grind 50 g. of molybdenite[1] and sift it through fine wire gauze; grind again all the powder that will not pass through the sieve, and continue the process until nothing remains behind. Roast the powder in a small evaporating dish, heating strongly with a Fletcher burner, and stirring frequently until the mass has been largely converted into yellow molybdenum trioxide and the sulphur has escaped as sulphur dioxide. Carried out in this manner the roasting consumes from four to six hours; if it is carried out in a porcelain tube, in which a better circulation of air is obtained, the same result is accomplished in from thirty minutes to an hour. The tube should be about 25 cm. long and 3 cm. in diameter, and should be placed in a slightly inclined position within an asbestos heating chamber (Fig. 4, p. 3).

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[1] Since molybdenite is difficult to pulverize the expedient recommended long ago by Scheele may be used. Cut it into small pieces with scissors and mix it with potassium sulphate crystals, the sharp edges of which under the pestle tear the flakes of the molybdenite apart; finally dissolve out the potassium sulphate with water.

Extract the roasted product with 2-normal ammonia solution, dry the dark-colored residue, roast it, and extract it again with ammonia; finally repeat the process once more, when nothing but a grayish gangue remains.

To the entire ammoniacal extract add three drops of ammonium sulphide to precipitate traces of copper; after standing twelve hours, filter, add a drop of bromine to the filtrate, and evaporate until crystallization takes place, adding at the last a few drops of concentrated ammonia. The addition of a little alcohol aids the separation of crystals. Dry the product in the air. Yield, 35 to 40 g. of small flake-like crystals; theoretical yield from pure molybdenite, 47.5 g.

A dilute solution of ammonium molybdate slightly acidified with hydrochloric acid, gives a dark-blue color when treated with one drop of stannous chloride; upon further addition of this reagent it becomes a dirty green. Dependent preparation: Molybdenum Blue, No. 24.

(*b*) *Oxides of Molybdenum.*

Molybdenum Trioxide, MoO_3. Ignite some ammonium molybdate at first gently and then strongly in an evaporating dish. The ignited product usually contains some lower oxide; to change this completely to the trioxide, place the material in a combustion tube and heat in a slow current of oxygen, using a row burner (Fig. 2) and covering the tube with an asbestos mantle. Do not heat the substance sufficiently to volatilize the molybdenum trioxide.

Molybdenum Dioxide, MoO_2. Place 2 g. of molybdenum trioxide in a weighed glass tube, about 35 cm. long, which has been drawn out a little at one end, and fill the tube with hydrogen which has been washed successively with caustic soda solution, silver nitrate, potassium permanganate, and sulphuric acid. Heat in the atmosphere of hydrogen for 15 minutes to moderate redness so that the temperature surely exceeds 470°. When cold, determine the loss in weight, and if necessary repeat the heating until finally the change in weight corresponds to the change from the trioxide to the dioxide. In this way a reddish-brown glistening powder is obtained.[1] Stronger ignition in hydrogen causes the formation of metallic molybdenum.

(c) *Chlorides of Molybdenum.*

Molybdenum Dioxydichloride, MoO_2Cl_2. Place 2 g. of molybdenum dioxide in a glass tube about 50 cm. long, and pass over it a current of chlorine which is dry and entirely free from air. After the air is completely expelled from the tube, heat gently by means of a Bunsen burner with a flame spreader. The volatile molybdic acid chloride sublimes and deposits as a loose mass of pinkish-white plates in the colder parts of the tube. After the reaction is ended replace the chlorine with dry carbon dioxide, and when cold, cut the tube at a point between the residue and the sublimed product. Transfer the crystals immediately to a glass-stoppered tube, since they are very hygroscopic, and make the stopper air-tight with a little vaseline.

Molybdenum Pentachloride, $MoCl_5$. First prepare the necessary metallic molybdenum by heating 15 g. of molybdenum trioxide in a current of hydrogen as hot as possible in a combustion furnace until no more water vapor is evolved. This method of reduction requires about three hours, and even then it is expedient to pulverize the product and to heat it a second time in hydrogen. Molybdenum reduced by the Goldschmidt method (see footnote below) may also be pulverized and used.

Meanwhile construct, under a hood with a strong draft, the apparatus represented in Fig. 26. Make as indicated two constrictions in the combustion tube so that at these points the inside diameter is from 1.0 to 1.2 cm., while the right-hand arm of the tube is 32 cm. and the left arm 60 to 70 cm. long.

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[1] Molybdenum dioxide, being non-volatile, is especially suited for the aluminothermic production of the fused metal. Place a mixture of 80 g. of molybdenum dioxide and 21 g. of aluminum powder in a clay crucible embedded in sand, and start the reaction by means of some fuse powder (cf. No. 2). Yield, 70 to 80%.

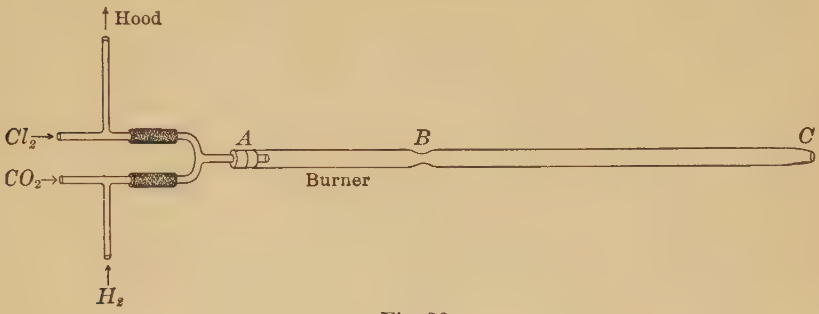

Fig. 26.

Place about 6 g. of powdered molybdenum in the shorter arm, and introduce carbon dioxide and hydrogen into the apparatus until all the air has been replaced in the wash bottles and the connections. Then close the pinch cock of the carbon dioxide tube, and, while passing a slow current of hydrogen, heat the molybdenum as strongly as possible with a row burner for one or two hours, preventing loss of heat by using the asbestos mantle. Drive out any condensed water through the open end of the tube, *C*, by fanning with a Bunsen flame. Allow the apparatus to cool completely while the hydrogen is still passing. Meanwhile start the action in the chlorine generator. Pass the chlorine gas through a wash bottle containing water, and then through two others containing concentrated sulphuric acid; at the outset, keep the rubber connector which admits to the combustion tube closed by means of a pinch cock, and allow the chlorine to escape as indicated through the side arm into the ventilating flue. When the air has been completely driven out of the evolution flask and from all the connections (which, with a fairly rapid current of chlorine, requires about an hour), replace the hydrogen in the combustion tube with carbon dioxide, and then the latter with chlorine. The reaction begins either of itself or on heating very gently with the row burner. Streams of a dull-red vapor rise and condense beyond the constriction at *B*. By heating the molybdenum gently with the row burner and occasionally playing a Bunsen flame over the constriction at *B*, bring the product into the section of the tube *BC* where it precipitates in a shower of very minute crystals. Avoid heating too strongly. At the end of the operation only a few gray flocks remain behind to the left of *B*. During the process the end of the tube at *C* is connected with a wide glass tube leading into the flue.

Allow the crystals to cool in a current of carbon dioxide, close *C* with a cork, and, with a blast lamp, fuse the tube together at *B*. By repeatedly tapping the tube loosen the crystals and transfer them to a preparation tube which is made ready as follows: Close one end of a fusible glass tube 35 cm. long and of the same width as the combustion tube, and make a constriction 20 cm. above the closed end. Fill the tube with carbon dioxide, and place the open end over the narrowed end *C* of the combustion tube. As soon as the substance is transferred seal the constricted part of the preparation tube. Dissolve the residue adhering within the combustion tube in alcohol; considerable heat is evolved, and an emerald-green solution is obtained which, when treated with ammonia, gives a grayish-brown flocculent precipitate.

Molybdenum Trichloride, $MoCl_3$. In an apparatus like that used for the preparation of the pentachloride, substitute a combustion tube prepared as shown in Fig. 27. The lengths of the three sections of the tube are 32 cm., 8 cm., and 60 to 75 cm. respectively, and the inside diameter at the constrictions *A*, *B*, and *C* is from 1.0 to 1.2 cm. Proceed at first, exactly as directed above, to prepare molybdenum pentachloride from 6 g. of molybdenum, and allow the greater part of this product to sublime into the longest section of the tube, while a small amount condenses in the 8 cm. section. Allow the tube to cool, replace the chlorine by carbon dioxide and the latter by hydrogen. Then place the combustion tube in a somewhat inclined position so that *D* is higher than *A*. Heat the tube at *C*, while a fairly strong current of hydrogen is passing, until the pentachloride

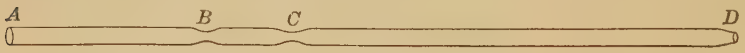

Fig. 27.

there vaporizes, and then continue to heat so that 5 to 10 cm. of the section *CD* remains constantly filled with red vapors. At first there is no evidence of chemical change; but after some time hydrogen chloride can be recognized in the escaping gases, and, on continuously vaporizing the pentachloride, which repeatedly condenses and flows back, a copper-red film is deposited, and gradually a mass of the same or often a darker color is produced. Carry the heating gradually towards *D* until finally all the pentachloride is converted to the trichloride; two to three hours are required for this. Too strong heating is to be avoided, for the lower the temperature at which the transformation takes place the better the preparation. Finally, replace the hydrogen by carbon dioxide and distil the remainder of the pentachloride from the 8 cm. section so that its vapor passes over the trichloride. Allow none of the pentachloride to remain with the preparation, but drive out all the excess at *D* after removing the escape tube which leads to the flue. Allow the preparation to cool, cut the tube into several pieces, and remove the crystals with a glass rod. Yield, 4 to 6 g. The product is not hygroscopic; it consists usually of a crystalline mass the color of red phosphorus but sometimes of feathery crystalline aggregates.

167. Tungsten Compounds from Wolframite.

The most common tungsten mineral is wolframite, which is essentially a mixture of manganous and ferrous tungstates.

(*a*) *Ammonium Tungstate*, $5\,(NH_4)_2WO_4 . 7\,WO_3 . 11\,H_2O$.

Boil 200 g. of finely powdered wolframite gently for about three hours in a 300-c.c. Erlenmeyer flask with 50 c.c. of concentrated hydrochloric acid and 10 c.c. of concentrated nitric acid; replace from time to time the acid as it evaporates. Then dilute the mass with a large amount of water and decant off the solution, which contains chiefly ferric and manganous chlorides, from the grayish-yellow easy-settling residue. Again boil the residue gently for two hours with the same mixture of acids and repeat the washing and decantation.

Dilute the decanted liquids to a volume of 1.0 to 1.5 liters, and if after several hours a yellow precipitate of tungstic acid separates, collect it on a filter after pouring off most of the liquid, and add it to the main insoluble residue.

Wash the insoluble residue, consisting of silicic acid, unattacked wolframite, and yellow tungstic acid, first with water containing a little hydrochloric acid, and then with pure water; transfer the powder to a beaker, and warm it on the water bath with enough 2-normal ammonia so that all of the tungstic acid passes into solution. Then filter and treat the residue with acids, etc., exactly as at first, in order to make certain that no large amount of the original mineral remains unattacked. Finally, unite all the ammoniacal extracts, filter the solution again, and concentrate it until crystals of ammonium tungstate begin to form. Then add 10 c.c. of concentrated ammonia and allow the solution to cool. Drain the colorless crystalline meal on a filter, and work up the mother liquor until only a very little remains. Dry the preparation in the hot closet. Yield, about 90 g.

A solution of ammonium tungstate gives a light-yellow precipitate with stannous chloride. The precipitate dissolves partly or wholly in concentrated hydrochloric acid, and, on heating the latter solution, a precipitate is thrown down which at first is dirty blue and later becomes pure dark blue.

(*b*) *Tungstic Acid and Tungsten Trioxide.*

Yellow Dibasic Tungstic Acid, H_2WO_4. Boil 3 g. of ammonium tungstate gently for five minutes in an evaporating dish with a mixture of 10 c.c. of concentrated hydrochloric acid and 5 c.c. of concentrated nitric acid. Allow the liquid to cool and dilute it with water. Collect the solid residue on a suction filter, wash it with hot water until the washings show a neutral reaction to blue litmus, and dry it in the hot closet. By igniting the tungstic acid it loses one molecule of water and is transformed into tungsten trioxide. Determine the loss in weight.

White Tungstic Acid, H_4WO_5(?). Dissolve 3 g. of ammonium tungstate in 30 c.c. of water with the addition of a few drops of ammonia. Then add to the solution at the room temperature an equal volume of 10% hydrochloric acid. White tungstic acid is thereby precipitated. After it settles, collect the solid and wash it with hot water containing some hydrochloric acid. If the filtrate is opalescent by reflected light, it contains colloidal tungstic acid which can be precipitated by gentle heating. Dry the preparation at a moderate temperature on top of the hot closet.

Tungsten Trioxide, WO_3. This oxide can be obtained by heating either of the above acids, or it can be formed directly from ammonium tungstate by heating the salt in a porcelain crucible at first over a Bunsen flame and finally over a blast lamp. The oxide is a lemon-yellow powder which in the sunlight acquires a greenish tinge.

(*c*) *Tungsten Hexachloride*, WCl_6.

First prepare metallic tungsten, as a grayish-black powder, by reducing the trioxide in an atmosphere of hydrogen at the highest temperature obtainable in the combustion furnace. (Cf. the preparation of molybdenum under Molybdenum Pentachloride, p. 224.)

Prepare tungsten hexachloride from the metallic tungsten according to the directions for obtaining molybdenum pentachloride from molybdenum (p. 224). Here also it is important to exclude moisture and atmospheric oxygen with the greatest care. On passing chlorine over the metal some yellow tungsten oxychloride is formed at first; expel this by heating the tube with a free flame, and allow the vapors to condense only when they have become dark colored. The hexachloride is a dark-violet, very hygroscopic, crystalline powder, which must be preserved in a sealed tube. Light and air change it to yellow tungstyl chloride, WO_2Cl_2.

168. Working Up of Pitchblende and Testing of the Components for Radioactivity.

Becquerel discovered in 1896 that pitchblende and uranium preparations send out peculiar radiations which, like the Roentgen rays, can be detected by their action upon photographic plates, and by their ability to make the air through which they pass a conductor of electricity. These radiations are called Becquerel rays, and the substances emitting them are said to be radioactive. By separating pitchblende into its constituents and by testing each for its radioactivity, M. and Mme. Curie (1898) established the fact that the ability to emit Becquerel rays becomes concentrated in certain definite constituents; the barium sulphate, which they prepared from the barium residues obtained in the technical working up of the ore, was found to be particularly active; and from this they succeeded in isolating a new element, radium, which showed to the very highest degree the property of radioactivity. The lead, bismuth, uranium, and rare earths obtained from pitchblende are also radioactive, although to a lesser degree.

Uranium compounds are obtained technically from pitchblende by digesting the ore with nitric acid, evaporating to dryness, and extracting the residue with water; uranyl nitrate is crystallized from the solution. The insoluble material is then extracted with a large amount of sodium carbonate solution, whereby the rest of the uranium is dissolved as sodium uranyl carbonate. The residues from this treatment form the starting material for obtaining radium.

This discovery of radium and radioactivity was epoch-making for both physics and chemistry. So intense has the investigation of radioactivity become that special journals giving original literature and references to all work performed in this field are now published both in English and German.

Pulverize 10 to 15 g. of pitchblende as finely as possible, and digest the powder for several hours on the water bath with a mixture of 20 g. of concentrated nitric acid and an equal amount of water. Evaporate the mixture to dryness, and treat the residue twice successively with 5 g. of the same acid mixture, evaporating each time to dryness. Extract the dry mass with water and evaporate the filtrate on the water bath. Place the dry residue from the aqueous solution in a flask, and extract it several times with warm ether until nothing more dissolves; evaporate the ethereal solution of uranyl nitrate, taking care that the vapor does not take fire. Dissolve the salt in water, precipitate it with ammonia, and ignite the precipitate to uranium octooxide, U_3O_8.

Treat with aqua regia the water-insoluble residue from the nitric acid treatment, and evaporate the mass to dryness. Moisten the residue with a little concentrated hydrochloric acid, extract it with hot water, and combine the solution with an aqueous solution of the residue left from the extraction with ether.

Separate the constituents of the solution thus obtained according to the usual procedure of qualitative analysis. The working up of the hydrogen sulphide precipitate yields: (1) As, Sb, Sn; (2) Pb; (3) Bi; (4) Cu. Dissolve the ammonium sulphide precipitate in hydrochloric acid, oxidize the solution, and precipitate Fe, Al, and the rare earths with ammonia. Treat this precipitate immediately with concentrated sodium carbonate solution, whereby the remainder of the uranium dissolves; it can be precipitated by caustic soda from this solution as sodium pyrouranate. Dissolve the residue from the sodium carbonate treatment in as little hydrochloric acid as possible, nearly neutralize the solution with ammonia, and then treat it with a solution of oxalic acid. This precipitates as oxalate any thorium that is present. On treating the filtrate with ammonia, the hydroxides of iron and aluminum are precipitated. The filtrate from the first precipitation with ammonia may contain zinc and cobalt; these metals should be precipitated with ammonium sulphide, but they need not be separated from each other.

The filtrate from the ammonium sulphide group, on being treated with ammonium oxalate, yields a precipitate of oxalates of the alkaline earth metals.

That part of the ore which does not dissolve in nitric acid nor during the subsequent treatment with aqua regia, should be fused in a porcelain crucible with a mixture of sodium and potassium carbonates. Extract the fusion with water, and wash the residue until the filtrate no longer gives a test for sulphate. Dissolve the carbonates in dilute nitric acid, and test the solution for lead and the alkaline earth metals. The combined alkaline earths should be separated from each other only when larger amounts of pitchblende are worked up.

Testing for Radioactivity.

(*a*) *Photographically.* Fold a piece of black paper around a photographic dry plate (in the dark room), so that the sensitive side is covered with one thickness of the paper, and place the whole in a box with the sensitive side up. Upon the plate arrange samples of the original pitchblende and of the different preparations obtained from it, each enveloped in a piece of paper. Record the position of each specimen and then close the box. Open it at the end of twenty-four hours and develop the plate in the usual manner.[1]

(*b*) *Electroscopically.* An approximate measure of activity can be obtained with the aid of a sensitive gold-leaf electroscope. A scale should be placed so that the distance between the gold leaves can be read. The top of the electroscope should consist of a metal plate, and above this at a definite distance a second metal plate that is connected with the earth should be supported. Charge the electroscope, and measure the conductivity of the layer of air between the two plates by determining the time required for the two leaves of the electroscope to reach the zero position. It is sufficient to observe over how many scale divisions the leaves pass within a certain length of time, e.g., the scale divisions per minute. To measure the activity, spread an amount of the substance, weighed to an accuracy of two figures, upon a piece of paper, and place the paper on the lower metal plate. Adjust the second plate in position, charge the electroscope, and make the readings. The quotient obtained by dividing the number of scale divisions traversed per minute by the weight of the substance, gives the specific activity. The observed rate may be corrected by subtracting from it the velocity with which the leaves come together in a blank experiment with none of the active preparation. If it is desired to compare the values obtained with those that have been published in the literature, the apparatus may be standardized by using uranyl nitrate.

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[1] Uranyl nitrate, when prepared as above by the ether method, does not show its full activity at once; its maximum intensity is "recovered" very slowly, — one-half in twenty-two days.

Of the active radiations, the part consisting of the so-called α-rays is held back by a sheet of paper. If, therefore, the experiment is repeated exactly as above, except that the preparation is covered with filter paper, the value then obtained corresponds to the activity of the rays that pass through the paper, that is, of the so-called β-rays. The difference between the two values gives the activity of the α-rays. Radioactive lead preparations emit principally α-rays.

169. Uranium Compounds.

As the starting material in the preparation of uranium compounds, either uranium nitrate prepared from pitchblende according to the following procedure, or the commercial product, may be used.

Uranyl Nitrate, $UO_2(NO_3)_2$. Heat 50 g. of finely powdered and sifted pitchblende in an evaporating dish with 150 c.c. of 30% nitric acid until the excess of acid has been expelled. Extract the mass with hot water, and evaporate the filtered solution to dryness on the water bath. Boil the dry residue repeatedly with ether in a small flask, and evaporate the ethereal extract to dryness, taking great care that the vapor does not take fire.[1] Recrystallize the last residue from water. Yield, about 35 g.

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[1] Cf. footnote 2, p 214.

Uranyl Hydroxide, $UO_2(OH)_2$.

The hydroxide of hexavalent uranium is amphoteric, that is, it has acidic as well as basic properties. With acids it forms the uranyl salts, e.g., $UO_2(NO_3)_2$; with bases it gives the difficultly soluble salts of pyro-uranic acid, e.g., $K_2U_2O_7$. For this reason the free uranyl hydroxide cannot be obtained by adding a solution of an alkali hydroxide to one containing a uranyl salt; it is prepared by heating uranyl nitrate with anhydrous alcohol.

Heat 20 g. of uranyl nitrate with 50 g. of absolute alcohol on the water bath in such a way that the alcohol evaporates slowly, but does not boil. After some time yellow uranyl hydroxide separates; add more alcohol and evaporate further. Finally, extract the precipitate with water, and dry it at a moderate temperature.

Alkali Pyro-uranates. To a solution of uranyl nitrate, add potassium hydroxide, sodium hydroxide, or ammonia until all of the uranium is just precipitated. Drain the precipitate, wash it carefully with water and dry it in the hot closet. Sodium pyro-uranate is prepared industrially, and is used in the manufacture of yellow-green fluorescent glass.

Ammonium Uranylcarbonate, $UO_2CO_3 \cdot 2\,(NH_4)_2CO_3$. Add a solution of ammonium carbonate carefully to a dilute solution containing 20 g. of uranyl nitrate until precipitation is just complete; an excess of the reagent dissolves the precipitate. Filter off the small, light-yellow crystals, and wash them successively with water, alcohol, and ether. On standing, the preparation loses ammonium carbonate.

Uranium Trioxide, UO_3. Dry some uranyl ammonium carbonate, or uranyl hydroxide, at 100°; then place it in a test-tube, and, while shaking, heat it in an oil or paraffin bath at 250° to 300° until the color has become brick-red.

Uranium Octo-oxide, U_3O_8. This oxide is obtained by igniting uranium trioxide (or any oxide of uranium), or, more conveniently, ammonium pyro-uranate, in a porcelain crucible; it is a dark-green powder.

Uranous Oxalate, $U(C_2O_4)_2$.

Uranyl salts are changed by reduction into uranous salts. The latter, however, are easily oxidized again, although the difficultly soluble uranous oxalate is relatively stable. A satisfactory reducing agent is the sodium salt of hyposulphurous acid, which can be procured in the form of a paste containing 50% of the salt.

Prepare a solution containing 25 g. of the reducing agent, and add this to a solution of 25 g. of uranyl nitrate in 100 c.c. of water until the solution is decolorized; a precipitate is formed which is at first brown in color but changes to a lighter shade. Dissolve the precipitate in hydrochloric acid, filter, and treat the filtrate with a hot solution of 15 g. of oxalic acid in 120 c.c. of water. About 26 g. of gray, finely-crystalline uranous oxalate are precipitated.

To purify the precipitate, dissolve it in a solution of neutral ammonium oxalate, using 6 g. of the latter salt and 100 c.c. of water for each 10 g. of uranous oxalate. Reprecipitate the salt from the filtered solution by adding hydrochloric acid. After some hours filter off the precipitate, wash it with water and with alcohol, and dry it in the hot closet. Yield, 9 g. from each 10 g. of the impure salt.

Ammonium Urano-oxalate, $(NH_4)_4[U(C_2O_4)_4]$. Digest 10 g. of uranous oxalate with a solution of 5 g. of neutral ammonium oxalate in 50 c.c. of water; filter off the excess of uranous oxalate, and precipitate the double salt from the filtrate by adding alcohol a little at a time. Allow the mixture to stand for one or two days, and then filter off the crystal meal which has by that time become coarser. Yield, 12 g.

Uranium Tetrachloride, UCl_4. Uranium tetrachloride is prepared in the apparatus described under No. 166 (*c*), by passing perfectly dry chlorine over a mixture of uranium oxide, U_3O_8, and one-eighth of its weight of ignited wood charcoal, the whole being heated as hot as possible in a combustion furnace. The principle is the same as that outlined under No. 52. Uranium tetrachloride condenses in the front part of the tube, and is freed from admixed pentachloride by heating it in a current of carbon dioxide at about 150°. In this way a very hygroscopic mass of greenish-black crystals is obtained. The tetrachloride dissolves in water with evolution of heat, and yields a green solution (cf. Uranous Oxalate).

170. Thorium Compounds from Monazite.

Thorium was first discovered by Berzelius in the rare Scandinavian minerals thorite and orangite. When the oxide of thorium became of industrial importance through its use in the Welsbach incandescent mantles, a more abundant source was sought.[1] This was found in the mineral monazite, a phosphate of the rare earths and of thorium, which contains 4 to 7% of thorium oxide and 50 to 60% of the rare earths, about one-half of the latter being cerium oxide. This mineral occurs frequently, although only in small amounts, in primary rocks; but it is found in some places concentrated in secondary deposits.

Add 100 g. of finely powdered monazite sand, a little at a time, to 150 g. of concentrated sulphuric acid which is heated to 200° in an evaporating dish upon a Babo funnel. Keep the mass at this temperature for half an hour after all of the mineral is added; then allow it to cool completely, and pour it very slowly with constant stirring into 300 c.c. of water, whereby the temperature must not be allowed to rise above 25° at any time. Filter off the residue.

Separation of Thorium. To the filtrate add in small portions a solution of 50 g. of oxalic acid in 500 c.c. of water until no further precipitate forms. Filter off the precipitate, and wash it first with water containing small amounts of oxalic and sulphuric acids, and finally with a little pure water. Yield, about 75 g.

Filter off the precipitate, and wash it first with water containing small amounts of oxalic and sulphuric acids, and finally with a little pure water. Yield, about 75 g.

Make the filtrate approximately neutral with sodium carbonate and again add oxalic acid to throw out thorium. This second precipitate is of one-third to one-fourth the quantity of the first, and is not entirely free from phosphates. It is well to set it aside and to work it up together with the fresh mineral when making the next preparation.

Boil up the moist oxalates with a solution of 230 g. of anhydrous sodium carbonate in one liter of water; the thorium dissolves as sodium thorium carbonate, while the rare earths remain behind as carbonates. Filter the warm liquid immediately, and acidify the filtrate with hydrochloric acid; 3 to 4 g. of thorium oxalate are precipitated.

In order to recover the remainder of the thorium from the mixture of insoluble carbonates, dissolve the latter in just the necessary amount of nitric acid, evaporate the solution to dryness on the water bath, dissolve the residue in hot water, and precipitate thorium hydroxide from the boiling solution by adding sodium thiosulphate.[1]

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[1] It is interesting to note that although one kilo of thorium nitrate was worth about $500 in 1894, the price had fallen to $4 in 1912. It is however $7.50 in 1928. (Price of potassium iodide about $7.)

To precipitate the rare-earths, add sodium carbonate to the filtrate from the thorium hydroxide, drain and wash the precipitate, and dry it in the hot closet. This product may be worked up according to No. 171.

Purification of the Thorium. Dissolve the thorium precipitates in hydrochloric acid, adding, if necessary, a little nitric acid; evaporate the solution to dryness, take up the residue in water, filter if necessary, and treat the solution at 60° with a solution of sodium thiosulphate. Collect the precipitate on a filter, wash it with water containing some ammonium nitrate (as it has a tendency to pass into colloidal solution), and ignite it to thorium dioxide.

Thorium Sulphate. Heat the thorium oxide with concentrated sulphuric acid in a porcelain crucible until the excess of acid has been expelled, moisten the residue with a few drops more of sulphuric acid and heat it as before, but avoid bringing it to a red heat. Pulverize the thorium sulphate, which should be free from acid salt, and add it gradually, with vigorous stirring, to five times its weight of ice-water. If, after a little while, a considerable residue remains undissolved, remove it and subject it again to the treatment with concentrated sulphuric acid.

By warming the filtered solution to 30—35°, thorium sulphate octohydrate, $Th(SO_4)_2 \cdot 8\ H_2O$, together with a little enneahydrate, $Th(SO_4)_2 \cdot 9\ H_2O$, is caused to separate. Maintain the solution at this temperature, and allow it to evaporate until all of the salt has separated. Drain the crystals, wash them with a little water, then with alcohol, and dry them at the room temperature.

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[1] The salts of quadrivalent thorium are more easily hydrolyzed than those of the tervalent rare-earth metals. Thus thorium hydroxide is precipitated while the salts of the trivalent metals remain unchanged. The principle of this separation is similar to that of the basic acetate method used in analytical chemistry.

According to another method, the solution is warmed to 60 to 70° together with an excess of a 10% hydrogen peroxide solution; the thorium and some cerium are thrown down in the form of a flocculent precipitate which can be easily filtered.

Atomic Weight Determination of Thorium. In order to illustrate the principle of an atomic weight determination by the sulphate method, prepare first some anhydrous thorium sulphate from about 2 g. of the above hydrated salt. Heat the crystallized salt to 400° in a weighed platinum crucible which is supported by a platinum triangle within a larger crucible. When the weight has become constant, the amount of the anhydrous thorium sulphate, a, is given by subtraction. Then ignite the crucible over the blast lamp until the weight has again become constant. This gives the weight of thorium dioxide, b. If the atomic weight of oxygen is taken at 16.00 and that of sulphur as 32.06, the atomic weight of thorium is obtained by solving for x in the expression:

$$\frac{x + 2 \cdot 32.06 + 8 \cdot 16.00}{x + 2 \cdot 16.00} = \frac{a}{b}.$$

171. Separation of the Rare Earths.

The rare earths form a group of very closely related sesquioxides, the separation and characterization of which for a long time offered considerable difficulties. The properties of the analogous compounds of these earths do not differ sharply enough from each other to permit a complete separation to be made in a single operation; but the slight gradations in the properties may in general be used to effect a satisfactory separation if a given process is systematically repeated again and again. When these slight gradations are taken into account, the rare earths fall into a classification which corresponds closely to their occurrence in nature.

The first distinction is made between the cerium earths and the yttrium earths. The latter were discovered by Gadolin at the end of the eighteenth century in a mineral found in a feldspar quarry near Ytterby, in Sweden, and afterwards named after him gadolinite. The cerium earths were discovered at the beginning of the last century by Berzelius and Hisinger in the mineral cerite which had previously been investigated by Scheele without success. Soon afterwards lanthanum and didymium were discovered in the first half of the nineteenth century by Mosander, a pupil and friend of Berzelius. This same investigator found that yttrium is accompanied by terbium and erbium. The separation of the earths was accomplished by two different processes which in a more perfected form serve even to-day as the standard methods. Of these processes, one rests upon differences in the basicity of the earths, as manifested in the varying hydrolytic and thermic dissociation of their salts; the second process rests upon differences in the solubility of the double salts. The cerium earths are more weakly basic and form more difficultly soluble potassium double sulphates than the yttrium earths. Cerium itself occupies a characteristic position, as it is the only member of the group from which two series of salts are derived: the cerous salts with tervalent cerium, and the ceric salts containing quadrivalent cerium.

For the qualitative characterization of the earths, the color of their salts is first of all of importance. Lanthanum and cerous salts are colorless, ceric salts are yellowish-red, erbium salts pink, didymium salts violet. It marked then the beginning of a new era in the history of the rare earths, when, in 1861, through the application of spectrum analysis, it became possible to measure exactly the color of salt solutions by means of their absorption spectra, and the color of glowing vapors by means of emission spectra. It was in this epoch that the discovery of the periodic system of the elements was made (1869), by the aid of which Mendelejeff first recognized the tervalency of the rare-earth metals and predicted the existence of the element scandium, which was later discovered by Nilson. Further investigation and the examination of new minerals has since that time added a number of elements to the group. In the presence of didymium Lecoq de Boisbaudran discovered samarium. In the group of the yttrium earths, which since the time of Mosander was studied especially by Bahr and Bunsen, ytterbium was discovered by Marignac, while Cleve added the elements holmium and thulium. Marignac also discovered gadolinium, which together with terbium and europium occupies an intermediate position between the cerium and yttrium earths. Finally, didymium was separated by von Welsbach in 1885 into praseodymium, the salts of which are green, and neodymium, whose salts are violet.

The most recent epoch dates from the technical application by von Welsbach of thorium and cerium oxides in the incandescent gas-lighting industry.

The following table gives a summary of the rare earths and their atomic weights:

Cerium earths.		Terbium earths.		Yttrium earths.	
Lanthanum, La	138.90	Europium, Eu	152.0	Scandium, Sc	45.10
Cerium, Ce	140.25	Gadolinium, Gd	157.26	Yttrium, Y	88.9
Praseodymium, Pr	140.92	Terbium, Tb	159.2	Erbium, Er	167.7
Neodymium, Nd	144.27			Ytterbium, Yt	173.6
Samarium, Sm	150.43				

Further details concerning the chemistry of the rare earths can be found in the articles by R. J. Meyer which are published in Abegg's Handbuch der anorganischen Chemie and in the monograph by R. J. Meyer and O. Hauser "Die Analyse der seltenen Erden und der Erdsäuren."

As raw material for the rare-earth preparations, the mixture of carbonates obtained in working up monazite sand (No. 170) may be used. The crude cerium carbonate, or cerium oxalate, that can be obtained on the market, furnishes practically the same mixture of the earths, since it usually contains 40 to 50% of cerium salt, 15 to 20% of lanthanum salt, 25 to 30% of didymium salt, and 5 to 8% of yttrium earths.

The cerium is precipitated, according to the method of Witt and Theel, by adding ammonium persulphate to a boiling solution of the nitrates; ceric sulphate is thereby formed, but this is partially hydrolyzed, and an insoluble basic salt precipitates. By neutralizing the acid set free by the hydrolysis, a complete precipitation is made possible, but on the other hand, it is necessary to keep the liquid slightly acid to prevent the other rare earths from precipitating with the cerium. All of the cerium is thrown down in this way, but it is contaminated with some lanthanum and didymium.

Lanthanum and didymium are thrown out of the filtrate as potassium double sulphates; the yttrium earths remain in solution and can be precipitated as oxalates by adding ammonium oxalate.

The products of this separation are then each further separated and purified.

Dissolve 100 g. of the raw material by warming it on the water bath in 200 g. of concentrated nitric acid. The crude carbonate dissolves very quickly, but, if cerium oxalate is used, the addition of fuming nitric acid is necessary to effect solution. Evaporate the solution on the water bath until it is of sirupy consistency, and then take it up in 1500 c.c. of water. Add 35 g. of ammonium persulphate to this solution and heat it to boiling in a large evaporating dish. Stir the liquid by means of a mechanical stirrer, and add powdered magnesium carbonate in small portions to the boiling mixture until finally Congo paper is no longer turned blue, although litmus is still reddened by the solution, — toward the last the magnesium carbonate should be added very cautiously. The reaction is complete when, even after boiling for five minutes, the liquid does not become acid to Congo paper, although it must still turn litmus red. About 40 g. of the magnesium carbonate are required. Allow the dull-yellow precipitate to settle, drain it on the suction filter while it is still warm, and wash it with hot water.

Test the filtrate for cerium as follows: To 2 c.c. of the solution add ammonium chloride and then ammonia; filter off and wash the precipitate and then dissolve it in 5 to 10 c.c. of hot concentrated potassium carbonate solution. Treat the solution with hydrogen peroxide and some ammonia, and warm it. A slimy precipitate is produced, and if cerium is present both the solution and the supernatant liquid are of an orange-yellow color; if cerium is absent the precipitate is white or a faint pink. The test is less sensitive if the original solution is warmed directly with hydrogen peroxide and sodium carbonate. If the above tests show that cerium is present, add more ammonium persulphate to the solution and precipitate the cerium as before by adding magnesium carbonate.

Bring the cerium-free filtrate to boiling in an evaporating dish, and, while stirring as before with the mechanical device, add powdered potassium sulphate (about 35 g. in all) until the didymium absorption bands can scarcely be detected spectroscopically in a filtered sample of the solution. In making this test, use a pocket spectroscope; fill a test-tube of 2 to 3 cm. diameter — or still better a parallel-walled vessel of the same thickness — with the solution and place it between the slit of the spectroscope and a Welsbach light. The most easily recognized of the absorption bands of didymium are those to the right and left of the sodium line. If the solution is almost free from didymium, drain the precipitate of the double sulphates, $M_2(SO_4)_3 \cdot 3\, K_2SO_4$, of didymium and lanthanum, and wash it with a dilute potassium sulphate solution.

Add ammonium oxalate to the filtrate, and after some hours wash the precipitate with cold water; this precipitate contains the remainder of the rare earths that were present in the monazite — chiefly the yttrium earths; these are not to be further separated.

(*a*) *Cerium Compounds.*

Working Up of the Cerium Precipitate.

Cerium may be readily purified from other metals by forming ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, which is difficultly soluble in nitric acid.

Weigh the dried cerium precipitate approximately, and boil it in an evaporating dish for 30 minutes with five times its weight of a 10% solution of sodium hydroxide. After letting the solution settle, decant off the liquid as completely as possible, and boil the residue with some fresh caustic soda solution. Pour off the solution again, and wash the residue by decantation with hot water, pouring all the liquid through a filter. Finally, collect the entire residue on the filter, wash it until free from soluble sulphate, and dry it in the hot closet.

Treat the ceric hydroxide thus obtained with 2.65 parts by weight of concentrated nitric acid (sp. gr. 1.4), filter the solution through an asbestos felt in a Gooch crucible, and add to the filtrate a hot solution of 0.39 parts of ammonium nitrate in

1.1 parts of water. Evaporate the solution on the water bath until it begins to crystallize, then, after 12 hours, drain the red crystals of the double nitrate and wash them with a little nitric acid. Evaporate the mother-liquor to obtain several further fractions of crystals, and collect each fraction by itself. From the last mother-liquor, precipitate the remaining cerium, together with the impurities, by diluting with water and adding oxalic acid.

Ignite a small portion from each of the crystal fractions on a porcelain crucible cover over the blast lamp. The residue of ceric oxide is pale yellow when the cerium preparation is pure; if didymium is present it is of a reddish to chocolate-brown color. Recrystallize the fractions that are shown to be impure by dissolving the double nitrate in 1.6 to 1.7 times its weight of 40% nitric acid (3 parts HNO_3, sp. gr. 1.4, and 2 parts H_2O).

For the successful preparation of ceric ammonium nitrate it is important to avoid reducing the tetravalent cerium. On this account the nitric acid which is used as solvent must be boiled for a short time in a flask in order to expel lower oxides of nitrogen.

Cerium Sulphides.

Sulphides of cerium can be prepared by igniting cerous sulphate in a stream of hydrogen sulphide. If the temperature remains below 720° the dark-brown disulphide CeS_2 is formed; but if it is kept at a bright red heat, dark cinnabar-red cerous sulphide, Ce_2S_3, is produced.

Add hydrogen peroxide to a boiling aqueous solution, containing 20 g. of ceric ammonium nitrate, until the liquid is decolorized; then add 7 g. of sulphuric acid and evaporate the solution to dryness. Place the residue in a short combustion tube and heat it in a stream of hydrogen sulphide which has been dried with calcium chloride. Heat the tube in a combustion furnace first to a dull red and later to a bright red, and occasionally revolve the tube on its long axis.

If cerous sulphide has been formed, the product dissolves in hydrochloric acid without residue; if the product contains cerium disulphide, free sulphur separates on this treatment. Test the hydrochloric acid solution with barium chloride to show whether the sulphate has been completely decomposed.

Cerous Chloride, $CeCl_3$.

Anhydrous cerous chloride is readily obtained from the sulphide by igniting the latter in a stream of hydrogen chloride gas.

First prepare cerium sulphide in the manner just described; allow the tube to partly cool, and pass through it a stream of thoroughly dry hydrogen chloride; then heat it again to dull redness. The transformation is complete when the preparation has become pure white.

Anhydrous cerous chloride forms a crystalline very hygroscopic mass.

Anhydrous Ceric Sulphate, $Ce(SO_4)_2$. Prepare ceric oxide by igniting ceric ammonium nitrate strongly; pulverize the oxide, and boil it with a large excess of concentrated sulphuric acid, whereby it is converted into the deep-yellow crystalline sulphate without being dissolved. Pour off the excess of acid, wash the residue by decantation with glacial acetic acid, drain it on a hardened filter paper, and dry it over lime in a vacuum desiccator. Ceric sulphate dissolves to a considerable extent but never completely in water; on boiling the dilute solution an insoluble basic salt is precipitated. This behavior is utilized, as has been shown, in the separation of cerium from the other rare earths.

(*b*) *Lanthanum Compounds.*

Lanthanum Carbonate from the Lanthanum-Didymium Precipitate. Boil up the precipitate of the potassium double sulphates with five parts of concentrated nitric acid in a porcelain casserole, and pour the entire mass into fifteen parts of boiling water. To the clear solution, which is colored violet by neodymium, add ammonium oxalate, — taking 0.7 to 0.8 g. to each 1.0 g. of the double salt, — neutralize the solution with ammonia, and after some time filter off the precipitate. Wash and dry the latter, and ignite it over a Fletcher burner in a porcelain or clay crucible, surrounded by a funnel to prevent loss of heat. Dissolve the brown oxide thus formed by heating on the water bath with as little concentrated nitric acid as possible, evaporate the solution to a sirupy consistency, and dissolve the nitrates in 1 liter of water.

To separate the didymium from the lanthanum, sift magnesium oxide very slowly through wire gauze into the solution of the nitrates, while this is kept boiling in a porcelain dish and is at the same time stirred with a mechanical stirrer. The didymium is precipitated together with a little lanthanum, but the greater part of the lanthanum remains in solution free from didymium. Control the separation by means of the spectroscope, and stop adding magnesium oxide when a filtered portion of the solution, in a layer 3 cm. thick, shows no trace of the didymium absorption bands.

Filter off and wash the precipitate and work it up for didymium as directed below under (*c*). Precipitate the lanthanum from the filtrate by means of ammonium carbonate solution, after first adding 10 g. of ammonium chloride. In order to remove all traces of magnesium, dissolve the precipitate in hydrochloric acid and reprecipitate it with ammonium carbonate.

Lanthanum Sulphate, $La_2(SO_4)_3 \cdot 9\,H_2O$. The ennea-hydrate of lanthanum sulphate is readily obtained from lanthanum oxide, which is itself prepared by igniting the carbonate. Following the directions given for the preparation of thorium sulphate (No. 170) treat the oxide with concentrated sulphuric acid, dissolve the anhydrous sulphate in ice-water, and then warm the solution.

Determine the atomic weight of lanthanum by the sulphate method (cf. p. 236).

Lanthanum Acetate, $La(C_2H_3O_2)_3 \cdot 3\,H_2O$. Ignite 5 g. of lanthanum carbonate in a platinum crucible, pulverize the oxide thus formed, and treat it in a flask with three times its weight of glacial acetic acid; a reaction takes place with strong evolution of heat, either of itself or upon gentle heating. Dissolve the resulting thick paste in as little water as possible, whereby only a very small residue remains, and evaporate the filtrate until crystallization takes place. Drain the crystals, wash them, first with 50% alcohol, and then with pure alcohol, and dry them in the hot closet.

Dependent preparation: Lanthanum Blue, No. 23.

Lanthanum Sulphide and Anhydrous Lanthanum Chloride can be prepared according to the methods given for the corresponding cerium compounds.

(c) *Didymium Compounds.*

Dissolve the didymium precipitate in as little warm nitric acid as possible, and treat the solution with magnesium oxide, as directed in the didymium-lanthanum separation, until the didymium lines are only just faintly visible. Drain and wash the resulting precipitate, dissolve it in hydrochloric acid, and reprecipitate the didymium with ammonium carbonate; in order to remove the last traces of magnesium, dissolve and again reprecipitate the didymium carbonate. The preparation thus obtained consists chiefly of the neodymium salt, and is consequently pink in color. A separation from praseodymium is not possible on a small scale.

Didymium Chloride with Alcohol of Crystallization, $DiCl_3 \cdot 3C_2H_5OH$. Ignite 5 g. of didymium carbonate in a platinum crucible, dissolve the powdered didymium oxide by boiling with a saturated solution of dry hydrogen chloride in anhydrous alcohol (about 50 c.c. are necessary), and filter the yellow solution, which has the consistency of thin sirup, through a felt of asbestos in a Gooch crucible. Saturate the filtrate with dry hydrogen chloride gas. Drain the large light-red crystals which separate in the course of several hours, and wash them with a little alcohol. Yield, 6 to 7 g.

Didymium Sulphide and Anhydrous Didymium Chloride can be prepared according to the methods given for the corresponding cerium compounds.

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$3SiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Si$

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